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Ueber die Schlichtheit der Abschnitte gewisser Potenzreihen

Von

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In seiner interessanten Arbeit hat Herr G. Szegö[1] den folgenden Satz bewiesen: Die Funktion

$$f(z)=a_0+a_1z+\cdots\cdots+a_nz^n+\cdots\cdots$$

sei regulär und schlicht im Kreise $|z|<1$. Dann sind sämtliche Abschnitte

$$S_n(z)=a_0+a_1z+\cdots\cdots+a_nz^n, \quad (n=1, 2,\cdots\cdots)$$

schlicht im Kreise $|z|<\frac{1}{4}$.

Daran anschliessend möchte ich hier die Potenzreihen

(1) $$f(z)=a_0+a_1z+\cdots\cdots+a_nz^n+\cdots\cdots$$

und ihre sämtlichen Abschnitte

(2) $$S_n(z)=a_0+a_1z+\cdots\cdots+a_nz^n, \quad (n=1, 2,\cdots\cdots)$$

betrachten, die mit den Bedingungen

(A) $$a_1\neq 0, \quad |a_1|\geqq|a_n|, \quad (n=2, 3,\cdots\cdots)$$

charakterisiert sind.

1. Bevor ich zu Potenzreihen vom Typus A——in den folgenden Zeilen bezeichne ich die Potenzreihen mit den Bedingungen (A) mit „Potenzreihen vom Typus A"——übergehe, beschäftige ich mich mit den Potenzreihen (1), die mit noch allgemeineren Bedingungen

(B) $$a_1\neq 0, \quad a_n=O(1)$$

bedingt sind.

Diese Potenzreihen sind regulär im Kreise vom Radius nicht

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1. G. Szegö: Zur Theorie der schlichten Abbildungen. Math. Annalen. **100**, (1928).

kleiner als Eins. Denn, da $f(z)$ vom Typus B ist, gibt es eine positive Zahl m derart, dass

$$|a_n| \leqq m, \quad (n = 1, 2, \cdots\cdots),$$

daher ist

$$r = \frac{1}{\overline{\lim_{n\to\infty}} \sup \sqrt[n]{|a_n|}} \geqq \frac{1}{\lim_{n\to\infty} \sqrt[n]{m}} = 1.$$

Nun ist für zwei verschiedene Punkte z_1, z_2 des Kreises $|z| < r$

$$\frac{f(z_1)-f(z_2)}{z_1-z_2} = a_1 + \sum_{\nu=2}^{\infty} a_\nu (z_1^{\nu-1} + z_1^{\nu-2}z_2 + \cdots\cdots + z_1 z_2^{\nu-2} + z_2^{\nu-1}).$$

Sei ρ die Schranke, die ich finden möchte, so ist für $|z_1| < \rho$, $|z_2| < \rho$

$$\left|\frac{f(z_1)-f(z_2)}{z_1-z_2}\right| > |a_1| - \sum_{\nu=2}^{\infty} \nu |a_\nu| \rho^{\nu-1}.$$

Da aber $f(z)$ vom Typus B ist,

$$\left|\frac{f(z_1)-f(z_2)}{z_1-z_2}\right| > |a_1| - m \sum_{\nu=2}^{\infty} \nu \rho^{\nu-1}.$$

Ferner ist

$$\sum_{\nu=2}^{\infty} \nu \rho^{\nu-1} = \frac{1}{(1-\rho)^2} - 1, \quad \text{für } \rho < 1,$$

so ist

$$\left|\frac{f(z_1)-f(z_2)}{z_1-z_2}\right| > |a_1| + m - \frac{m}{(1-\rho)^2}. \tag{3}$$

In analoger Weise hat man

$$\left|\frac{S_n(z_1)-S_n(z_2)}{z_1-z_2}\right| > |a_1| + m - \frac{m}{(1-\rho)^2}. \tag{4}$$

Deswegen sind für ρ, für das die Gleichung

$$|a_1| + m - \frac{m}{(1-\rho)^2} = 0 \tag{5}$$

genügt, die rechten Seiten von (3) und (4) beide positiv, d. h., für

$$\rho = 1 - \frac{\sqrt{m}}{\sqrt{|a_1| + m}},$$

woraus folgt der

Satz I. Es sei $f(z)$ regulär im Kreise $|z|<r$. Dann sind $f(z)$ und ihre sämtlichen Abschnitte schlicht im Kreise

$$|z| < 1 - \frac{\sqrt{m}}{\sqrt{|a_1| \quad m}},$$

falls $f(z)$ vom Typus B ist.

Wenn man hier setzt

$$m \quad |a_1|,$$

so erhält man eine Potenzreihe vom Typus A. Damit hat man den

Satz 2. Es sei $f(z)$ regulär im Kreise $|z|<r$. Dann sind $f(z)$ und ihre sämtlichen Abschnitte schlicht im Kreise

$$|z| < 1 - \frac{1}{\sqrt{2}} = 0.292\cdots\cdots,$$

falls $f(z)$ vom Typus A ist.

Ist die Potenzreihe (1) bedingt mit

(C) $\qquad |a_n| \geqq |a_{n+1}|, \quad (n = 1, 2, \cdots\cdots),$

so ist offenbar

$$|a_1| \geqq |a_n|, \quad (n = 2, 3, \cdots\cdots).$$

Also ergibt sich hieraus als spezieller Fall des Satzes 2 folgender Satz.

Es sei $f(z)$ regulär im Kreise $|z|<r$, so sind $f(z)$ und ihre sämtlichen Abschnitte $S_n(z)$ schlicht im Kreise

$$|z| < 1 - \frac{1}{\sqrt{2}},$$

falls $f(z)$ vom Typus C ist.

Dies ist der Satz, der von Herrn T. Itihara[1] bewiesen wurde.

2. Nun gebe ich zwei Sätze, die unmittelbar aus dem Satz I folgen.

Satz 3. Es sei

$$f(z) = a_0 + a_1 z + \cdots\cdots + a_n z^n + \cdots\cdots \qquad a_1 \neq 0$$

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1. T. Itihara: Eine Bemerkung über die Schlichtheit der Potenzreihe und ihrer Abschnitte. Japanese Jour. of Math. **6**, (1929).

regulär im Kreise $|z|<1$, so sind $f(z)$ und ihre sämtlichen Abschnitte schlicht im Kreise

$$|z|<1-\frac{1}{1/|a_1|+1},$$

falls $|f(z)|\leqq 1$ für $|z|<1$.

Nach dem von Cauchy herrührenden Satz sind

$$|a_n|\leqq 1, \quad (n=0, 1, \cdots\cdots).$$

Also ist $f(z)$ vom Typus B, daraus folgt die Behauptung.

Herr C. Carathéodory[1] hat den Satz bewiesen, welcher lautet[2]: Die Funktion

$$f(z)=\frac{1}{2}+a_1z+\cdots\cdots+a_nz^n+\cdots\cdots$$

sei im Kreise $|z|<1$ regulär und habe dort positiven Realteil. Dann sind

$$|a_n|\leqq 1, \quad (n=1, 2, \cdots\cdots).$$

Hierbei skizziere ich den Beweis flüchtig.

Man setze

$$a_n=\lambda_n+i\mu_n, \quad \lambda_n, \ \mu_n \text{ reell}$$
$$z=re^{i\vartheta}, \quad 0\leqq\vartheta<2\pi, \quad 0<r<1,$$

so ist

$$f(z)=\frac{1}{2}+\sum_{n=1}^{\infty}(\lambda_n\cos n\vartheta-\mu_n\sin n\vartheta)r^n+i\sum_{n=1}^{\infty}(\lambda_n\sin n\vartheta+\mu_n\cos n\vartheta)r^n.$$

Bezeichnet man mit $P(r,\vartheta)$ den Realteil der Funktion, so ist

$$P(r,\vartheta)=\frac{1}{2}+\sum_{n=1}^{\infty}(\lambda_n\cos n\vartheta-\mu_n\sin n\vartheta)r^n.$$

Daraus folgt

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1. C. Carathéodory: Ueber den Variabilitätsbereich der Fourierschen Konstanten von positiven harmonischen Funktionen. Rendiconti del Circolo Matematico di Palermo. **32**, (1911).

2. Ich habe hier die Wortlaute von Herren Pólya und Szegö benutzt, die in dem von ihnen herausgegebenen Buche „Aufgaben und Lehrsätze" vorhanden sind.

$$a_n=\lambda_n+i\mu_n=\frac{1}{\pi r^n}\int_0^{2\pi}P(r,\vartheta)e^{-in\vartheta}d\vartheta.$$

Demnach ist

$$|a_n|\leqq\frac{1}{\pi r^n}\int_0^{2\pi}P(r,\vartheta)d\vartheta$$

$$=\frac{1}{r^n}.$$

Hierbei lasse man r gegen 1 konvergieren.

Mit Hilfe dieses Satzes kann man den Satz ableiten:

Satz 4. Es sei

$$f(z)=\frac{1}{2}+a_1z+\cdots\cdots+a_nz^n+\cdots\cdots,\quad a_1\neq 0$$

regulär und habe positiven Realteil im Kreise $|z|<1$. Dann sind $f(z)$ und ihre sämtlichen Abschnitte schlicht im Kreise

$$|z|<1-\frac{1}{\sqrt{|a_1|+1}}.$$

Man sieht mit Hilfe des Carathéodoryschen Satzes, dass $f(z)$ vom Typus B ist. So folgt diese Behauptung unmittelbar nach dem Satz I.

3. Nun gehe ich zu schlichten Potenzreihen über.

Hilfssatz I (von Herrn Szegö)[1].

Es sei

$$f(z)=a_0+a_1z+\cdots\cdots+a_nz^n+\cdots\cdots$$

regulär und schlicht im Kreise $|z|<1$. Dann gilt für $|z_1|<1$, $|z_2|<1$ die Ungleichung

$$\left|\frac{f(z_1)-f(z_2)}{z_1-z_2}\right|\geqq|a_1|\left(\frac{1-|z_1|}{1+|z_1|}\right)^2\frac{|1-\bar{z}_1z_2|}{(|1-\bar{z}_1z_2|+|z_1-z_2|)^2}.\tag{6}$$

Beweis. Wie man leicht nachprüft, ist

$$\varphi(\zeta)=\frac{f(z_1)-f\left(\frac{-\zeta+z_1}{1-\bar{z}_1\zeta}\right)}{f'(z_1)(1-|z_1|^2)}$$

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1. G. Szegö. loc. cit. Mit Hilfe des Kunstgriffes, der in dem von Herrn L. Bieberbach bearbeiteten „Lehrbuch der Funktionentheorie" vorhanden ist, habe ich im Beweise geringe Modifikation gemacht.

auch im Kreise $|\zeta|<1$ regulär und schlicht und besitzt eine in $|\zeta|<1$ gültige Potenzreihenentwicklung, die so beginnt

$$\varphi(\zeta)=\zeta+\gamma_2\zeta^2+\cdots\cdots.$$

Es sei hier

$$z_2=\frac{-\zeta_2+z_1}{1-\bar{z}_1\zeta_2}, \quad \text{wo } |\zeta_2|<1 \text{ ist, damit ist } |z_2|<1,$$

so ist

$$\left|\frac{f(z_1)-f(z_2)}{f'(z_1)(1-|z_1|^2)}\right|\geqq\frac{|\zeta_2|}{(1+|\zeta_2|)^2}.$$

Also ist

$$\left|\frac{f(z_1)-f(z_2)}{z_1-z_2}\right|\geqq|f'(z_1)|(1-|z_1|^2)\cdot\frac{|1-\bar{z}_1z_2|}{(|1-\bar{z}_1z_2|+|z_1-z_2|)^2}.$$

Da aber

$$|f'(z_1)|\geqq|a_1|\frac{1-|z_1|}{(1+|z_1|)^3}$$

ist, so folgt die Behauptung.

Hilfssatz 2. Es sei $f(z)$ vom Typus A. Setzt man

$$f(z)=S_n(z)+\sigma_n(z),$$

wo

$$S_n(z)=a_0+a_1z+\cdots\cdots+a_nz^n$$

und

$$\sigma_n(z)=a_{n+1}z^{n+1}+\cdots\cdots,$$

so gilt die Ungleichung

$$(7)\qquad \left|\frac{f(z_1)-f(z_2)}{z_1-z_2}\right|>\left|\frac{\sigma_n(z_1)-\sigma_n(z_2)}{z_1-z_2}\right|,$$

für $|z_1|<\frac{1}{3}$, $|z_2|<\frac{1}{3}$ und $n\geqq4$.

Beweis. Nach dem Hilfssatz I ist

$$\left|\frac{f(z_1)-f(z_2)}{z_1-z_2}\right|\geqq|a_1|\left(\frac{1-|z_1|}{1+|z_1|}\right)^2\cdot\frac{1}{|1-\bar{z}_1z_2|+2|z_1-z_2|+\left|\frac{(z_1-z_2)^2}{1-\bar{z}_1z_2}\right|}.$$

Ich unterscheide zwei Fälle:

i) $|z_1 - z_2| \geqq 0.2.$

Man hat

$$\left|\frac{1-\bar{z}_1 z_2}{z_1 - z_2}\right| < 5 \cdot \left(1 + \frac{1}{9}\right) = \frac{50}{9}$$

und

$$\left|\frac{z_1 - z_2}{1-\bar{z}_1 z_2}\right| < 1.$$

Daher ist

$$\left|\frac{1-\bar{z}_1 z_2}{z_1 - z_2}\right| + 2 + \left|\frac{z_1 - z_2}{1-\bar{z}_1 z_2}\right| < 3 + \frac{50}{9} = \frac{77}{9},$$

woraus folgt

$$|a_1|\left(\frac{1-|z_1|}{1+|z_1|}\right)^2 \cdot \frac{1}{|1-\bar{z}_1 z_2| + 2|z_1 - z_2| + \left|\frac{(z_1-z_2)^2}{1-\bar{z}_1 z_2}\right|}$$

$$> \frac{|a_1|}{|z_1 - z_2|} \times \frac{1}{4} \cdot \frac{9}{77}$$

$$> \frac{|a_1|}{|z_1 - z_2|} \times 0.029.$$

Da aber $f(z)$ vom Typus A ist, so ist

$$\left|\sum_{\nu=n+1}^{\infty} a_\nu \frac{z_1^\nu - z_2^\nu}{z_1 - z_2}\right| \leqq \frac{|a_1|}{|z_1 - z_2|} \sum_{\nu=n+1}^{\infty} |z_1^\nu - z_2^\nu|$$

$$< \frac{|a_1|}{|z_1 - z_2|} 2 \cdot \sum_{\nu=n+1}^{\infty} \left(\frac{1}{3}\right)^\nu$$

$$< \frac{|a_1|}{|z_1 - z_2|} \times 0.013, \text{ für } n \geqq 4.$$

ii) $|z_1 - z_2| < 0.2.$

Man hat wieder

$$|1 - \bar{z}_1 z_2| < 1 + \frac{1}{9} = \frac{10}{9}$$

$$2|z_1 - z_2| < \frac{2}{5}$$

und

$$\left|\frac{(z_1-z_2)^2}{1-\bar{z}_1z_2}\right|<\frac{1}{25}\cdot\frac{1}{1-\frac{1}{9}}=\frac{9}{200}.$$

Daher hat man

$$|1-\bar{z}_1z_2|+2|z_1-z_2|+\left|\frac{(z_1-z_2)^2}{1-\bar{z}_1z_2}\right|<\frac{10}{9}+\frac{2}{5}+\frac{9}{200}$$

$$=\frac{2801}{1800}.$$

Daraus folgt

$$|a_1|\left(\frac{1-|z_1|}{1+|z_1|}\right)^2\cdot\frac{1}{|1-\bar{z}_1z_2|+2|z_1-z_2|+\left|\frac{(z_1-z_2)^2}{1-\bar{z}_1z_2}\right|}$$

$$>|a_1|\times\frac{1}{4}\cdot\frac{1800}{2801}$$

$$>|a_1|\times 0.16.$$

Ferner ist

$$\left|\sum_{\nu=n+1}^{\infty}a_\nu\frac{z_1^\nu-z_2^\nu}{z_1-z_2}\right|<|a_1|\sum_{\nu=n+1}^{\infty}\nu\left(\frac{1}{3}\right)^{\nu-1}$$

$$=|a_1|\times\frac{11}{108},\quad \text{für } n\geqq 4,$$

$$<|a_1|\times 0.102.$$

Also ist die Behauptung bewiesen.

Satz 5. Es sei $f(z)$ regulär und schlicht im Kreise $|z|<1$, dann sind sämtliche Abschnitte schlicht im Kreise

$$|z|<\frac{1}{3}=0.333\cdots\cdots,$$

falls $f(z)$ vom Typus A ist.

Beweis. Es ist

$$\left|\frac{S_n(z_1)-S_n(z_2)}{z_1-z_2}\right|>\left|\frac{f(z_1)-f(z_2)}{z_1-z_2}\right|-\left|\frac{\sigma_n(z_1)-\sigma_n(z_2)}{z_1-z_2}\right|.$$

Nach dem Hilfssatz 2 ist für $n\geqq 4$

$$\left|\frac{f(z_1)-f(z_2)}{z_1-z_2}\right|>\left|\frac{\sigma_n(z_1)-\sigma_n(z_2)}{z_1-z_2}\right|, \text{ wo}$$

$$|z_1|<\frac{1}{3}, \quad |z_2|<\frac{1}{3}.$$

Für $n=3$ und $n=2$ ist die Behauptung leicht zu beweisen.
Für $n=3$ ist

$$|a_1+a_2(z_1+z_2)+a_3(z_1^2+z_1z_2+z_2^2)|$$
$$\geqq|a_1|-|a_2(z_1+z_2)+a_3(z_1^2+z_1z_2+z_2^2)|.$$

Da aber $f(z)$ vom Typus A ist, ist

$$\geqq|a_1|\{1-(|z_1|+|z_2|)-(|z_1|^2+|z_1||z_2|+|z_2|^2)\}$$
$$>|a_1|\left(1-\frac{2}{3}-\frac{1}{3}\right)=0.$$

Für $n=2$ ist

$$|a_1+a_2(z_1+z_2)|\geqq|a_1|\{1-(|z_1|+|z_2|)\}$$
$$>|a_1|\left(1-\frac{2}{3}\right)>0.$$

Damit ist der Satz vollständig bewiesen.

4. Die hiermit gewonnene obere Schranke $\frac{1}{3}$ für die Schlichtheit sämtlicher Abschnitte aller im Einheitskreise schlichten Potenzreihen vom Typus A scheint mir kaum die wahre obere Schranke zu sein.

Herr L. Fejér[1] hat den Satz bewiesen:

Das Polynom

$$1+z+\cdots\cdots+z^n \tag{9}$$

wo $n\geqq1$, ist im Kreise $|z|<\rho_n$ schlicht, wenn ρ_n die einzige positive Wurzel der Gleichung

$$1-(n+1)\rho^n-n\rho^{n+1}=0 \tag{10}$$

bezeichnet.

Ich sehe hierbei das Polynom als die Abschnitte der im Einheitskreise schlichten Potenzreihe

$$1+z+\cdots\cdots+z^n+\cdots\cdots \tag{11}$$

an. So ist die Potenzreihe (11) vom Typus A, daher müssen nach dem

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1. L. Fejér: Ueber die Grenzen der Abschnitte gewisser Potenzreihen. Acta litterarum ac scientiarum. **4**, (1928).

Satz 5 ihre sämtlichen Abschnitte im Kreise $|z|<\frac{1}{3}$ schlicht sein. In den folgenden Zeilen aber beweise ich einen Satz und mit dessen Hilfe schliesse ich, dass sämtliche Abschnitte

$$(9') \qquad 1+z+\cdots\cdots+z^n, \quad (n=1, 2, \cdots\cdots)$$

in ein wenig grösseren Kreise schlicht sind.

Hilfssatz 3. Versteht man unter ρ_n die positive Wurzel der trinomischen Gleichung

$$(10) \qquad 1-(n+1)\rho^n-n\rho^{n+1}=0,$$

so ist

$$\rho_2<\rho_3<\cdots\cdots<\rho_n<\cdots\cdots$$

und

$$\lim_{n\to\infty}\rho_n=1.$$

Beweis. Nach der Voraussetzung sind

$$(12) \qquad n\rho_n^{n+1}+(n+1)\rho_n^n=1$$

und

$$(13) \qquad (n+1)\rho_{n+1}^{n+2}+(n+2)\rho_{n+1}^{n+1}=1.$$

Aus der Relation (12) ist

$$(14) \qquad \frac{\rho_n}{n+1}+\frac{1}{n}=\frac{1}{n(n+1)\rho_n^n},$$

daraus folgt

$$\rho_n=\frac{1}{n\rho_n^n}-\frac{n+1}{n}.$$

In analoger Weise hat man

$$\rho_{n+1}=\frac{1}{(n+1)\rho_{n+1}^{n+1}}-\frac{n+2}{n+1}.$$

Wäre nun

$$\rho_n>\rho_{n+1},$$

so wäre

$$\frac{1}{n\rho_n^n}-\frac{n+1}{n}>\frac{1}{(n+1)\rho_{n+1}^{n+1}}-\frac{n+2}{n+1},$$

oder

$$\frac{1}{n\rho_n^n}-\frac{1}{(n+1)\rho_{n+1}^{n+1}}>\frac{1}{n(n+1)}.$$

Wegen der Relation

$$\frac{1}{\rho_n} < \frac{1}{\rho_{n+1}}$$

würde

$$\frac{1}{n\rho_n^n} - \frac{1}{(n+1)\rho_n^{n+1}} > \frac{1}{n(n+1)}$$

sein. Aus der Relation (14) aber sind

$$\frac{1}{n\rho_n^n} = \rho_n + \frac{n+1}{n}$$

und

$$\frac{1}{(n+1)\rho_n^{n+1}} = \frac{1}{\rho_n} + \frac{n}{n+1}.$$

Daher müsste

$$\rho_n - \frac{1}{\rho_n} > -\frac{2}{n+1}$$

sein, d. h.

$$\rho_n^2 + \frac{2}{n+1}\rho_n - 1 > 0,$$

woraus folgte

$$\rho_n > \frac{\sqrt{1+(n+1)^2}-1}{n+1}.$$

Man hat aber aus der Relation (12)

$$n\rho_n^{n+1} + (n+1)\rho_n^{n+1} < 1,$$

daher ist

$$\rho_n < \frac{1}{(2n+1)^{\frac{1}{n+1}}}.$$

Wie man leicht nachrechnet, ist

$$\frac{\sqrt{1+(n+1)^2}-1}{n+1} > \frac{1}{(2n+1)^{\frac{1}{n+1}}}, \quad \text{für } n \geqq 2,$$

was führt *ad absurdum*.

Dass ρ_n gegen 1 konvergiert, kann folgendermassen bewiesen werden. Aus der Relation (12) hat man

$$\rho_n^n = \frac{1}{n\rho_n + n + 1},$$

daraus folgt

$$n \log \rho_n = -\log (n\rho_n + n + 1).$$

Damit ist

$$\lim_{n\to\infty} \log \rho_n = 0,$$

d. h.

$$\lim_{n\to\infty} \rho_n = 1.$$

Also ist der Hilfssatz bewiesen.

Hinsichtlich dieses Hilfssatzes kann man behaupten:

Satz 6. Es seien

$$1 + z + \cdots\cdots + z^n, \quad (n = 1, 2, \cdots\cdots)$$

Abschnitte der Potenzreihe

$$1 + z + \cdots\cdots + z^n + \cdots\cdots,$$

dann sind diese sämtlichen Abschnitte schlicht im Kreise $|z| < \frac{1}{2}$. Diese Schranke kann durch keine grösseren Werte ersetzt werden, weil

$$1 + z + z^2$$

$\frac{1}{2}$ als die genaue Schranke für Schlichtheit hat.

Also aus der Sätze 5 und 6 erhalte ich schliesslich den Satz:

Unter die Potenzreihen, die im Einheitskreise regulär-schlicht und vom Typus A sind, gibt es eine Potenzreihe, deren sämtlichen Abschnitte im Kreise $|z| < \tau$ schlicht sind, wo

$$\frac{1}{3} < \tau < \frac{1}{2}$$

ist.

Zum Schlusse bemerke ich, dass ich dem Herrn Prof. Toshizô Matsumoto für seine Bemerkung und Anregung zu Dank verpflichtet bin.

The Crystal of Zinc coating the Surface of Iron Plate

By

Yoshiaki Matsunaga

(Received September 10, 1931)

Abstract

The writer examined the zinc crystal deposited on the surface of iron plate roentgenographically, to see whether it consisted of a zinc single crystal or whether it had some other special structure; and it was found that the zinc crystal deposited on the surface of iron plate, consisted of a single crystal of zinc, and that the basal plane (0001) of the hexagonal closed packed zinc crystal was inclined to the surface of the iron plate at an angle of about 18°.

The orientation of single crystals of zinc, formed under various conditions, has been investigated by K. Tanaka[1], but the orientation of the zinc crystal deposited on the surface of iron plate has not yet been examined.

In this investigation, the writer examined the following three kinds of specimens: (1) the zinc crystal formed on the surface of an iron plate of about 4.5 mms. in thicknesss, (2) the portion of the zinc crystal formed in the region beyond the edge of the iron plate, and (3) the iron plate itself on whose surface the zinc crystal was deposited. These test pieces were examined by taking the X-ray diffraction patterns.

The determination of the orientation of the crystal by means of the Laue-photograph was much faciliated by the use of the crystallographic globe devised by Prof. U. Yoshida[2].

1. K. Tanaka, These Memoirs, **11**, 361. (1928)
2. U. Yoshida, Japanese J. Phys. **4**, 133 (1927); S. Takeyama, These Memoirs, **12**, 257 (1929)

There are four methods for plating iron plate with zinc: the hot dipping, electro-galvanizing, spheradizing and metal spraying processes. As the first of these four methods, is the one generally used, it was also used in this experiment.

A piece of commercial zinc was melted in a crucible. Small pieces of commercial iron plate coated with zinc, 2—4 cms. in width and 4 cms. in length, were dipped into the molten zinc metal. Before they were dipped into it, their surfaces were cleaned with dilute sulphuric acid. The reason why the writer used commercial iron plate coated with zinc instead of iron plate itself is as follows. With an iron plate, the cleaning of its surface is very troublesome, but when an iron plate coated with zinc is dipped into molten zinc, the zinc film on the surface of the iron plate is immediately removed by being melted into it. Thus the deposit of zinc, which is formed on the surface of the plate when it is taken out of the melt, is considered to be formed on the surface of the iron plate, and not on the surface of the thin film of zinc which has coated the iron plate. So the trouble of cleaning the surface of the iron plate is avoided by this method.

The size of the crystals of zinc formed on the iron plate depends upon the cooling conditions. In general, when the plate is cooled slowly by using a large piece of it, we get large size crystals; but when it is cooled rapidly by using a small piece of it, small crystals appear on the surface of the plate.

When the plate was taken out of the molten zinc, the arrangement of the zinc crystals on the surface of the plate could not be seen clearly by the naked eye, so the surface of the plate coated with zinc was etched slightly with dilute sulphuric acid.

In order to examine, with X-rays, the crystals of zinc deposited on the surface of the iron plate in the manner described above, we must separate the zinc film on one side of the plate from the remaining part of the plate. To do this one side of the plate was covered with paraffin, and the remaining part of the plate was etched off with dilute hydrochloric acid. However the zinc film was so thin in our case, that it was very difficult to etch off the iron core completely from the zinc film.

To get over this difficulty, the method of preparing the specimens was slightly modified. An iron plate coated with zinc was dipped into the molten zinc, and when it was lifted slowly in the vertical direction from the molten zinc, a tongue-shaped part of zinc was formed

at the lower edge of the iron plate. This part of zinc was confirmed, by taking Laue-photographs, to belong to the same single crystal of zinc as that covering the lower part of the iron plate. The Laue-photograph reproduced in Fig. 2 of the plate is taken with the zinc crystal forming the tongue-shaped part at the lower edge of the iron plate as is stated above. Fig. 3 in the plate is the Laue-photograph taken with the iron core, prepared by etching off the zinc coatings on both sides of the plate; and Fig. 1 in the same plate is the Laue-photograph of the iron plate coated with zinc on one side, obtained by etching off the zinc-coating on the other side of the plate. By comparing the photographs in Figs. 1 and 3 in the plate, we can select the Laue-spots due to the zinc crystals in Fig. 1 of the plate. And the comparison and the determination of the orientations of the zinc-crystals in the cases of Figs. 1 and 2 in the plate are thus performed promptly by the aid of the crystallographic globe.

Table

No. of specimen	Angle between the surface of the iron plate and the crystal face (0001)
1	18°
2	18°
3	18°
4	18°

The orientation of the zinc crystals coating the iron plate, which is determined in the manner described above, is given in the Table. From this Table we know that the hexagonal zinc crystals coating the iron plate have such an orientation that their (0001)-plane is inclined to the surface of the iron plate at an angle of about 18°.

In conclusion, the writer wishes to express his sincere thanks to Prof. U. Yoshida, of Kyoto Imperial University for his guidance in the research.

Physical Laboratory,
The Nagoya Commercial College.
May 18, 1931.

Plate

Fig. 1

Fig. 2

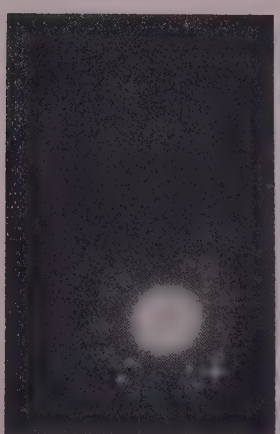


Fig. 3

On the Hydrolysis of Polysaccharides, I The Influence of Neutral Salts on the Acid Inversion of Sucrose

By

Shigeru Komatsu and **Gonichi Nomura**

(Received September 14, 1931)

In a course of the study of polysaccharides in our laboratory, the hydrolytic velocity of sucrose by the mineral acids was noticed to be modified to some extent by the presence of their salts, and the present communication deals with the experimental results.

In connection with the catalytic hydrolysis of sucrose in acid solution, especially in the presence of neutral salts, a large amount of research work has been done to confirm that the salts exert an influence on the reaction, and most of the investigators have attempted to explain this phenomenon in terms of the activity of the hydrogen ions in the reaction system[1].

According to H. Colin and A. Chandun the velocity of the hydrolysis of sucrose by HCl in the presence of neutral salts (KCl, KBr) depends not only upon the concentration of the salts but on that of the sucrose[2].

A solution of 20 gms. of purified sucrose was mixed with sulphuric acid and the salts, which diluted to 100 c.c. would give their desired concentration. The solution was transferred to the polarimeter tubes, and the readings taken at different time intervals, the temperature being maintained at 25°, 30° and 35°.

The reaction velocity constants were calculated according to the

1. Caldwell: Report Brit. Assoc. Adr. Sci., (1906) 267; W. C. Mc Lewis: Trans. Faraday Soc., **17**, 573 (1922); C. F. Kantz & A. L. Robinson: Jour. Am. Chem. Soc., **50**, 1023 (1928).

2. C. R., **192**, 1929 (1931).

formula: $K=\frac{2.30}{t}\log\frac{a_0-a_\infty}{a-a_\infty}$,

t being the time in minutes, a_0 the initial rotation, a the rotation at a time t, a_∞ the final rotation.

20 % Sucrose, $\frac{N}{1}$ H_2SO_4, t=25°.

Time in minutes	α	K
0	6.68°	
81	5.33	0.00212
106	5.00	206
126	4.38	248
169	4.00	222
204	3.53	225
267	2.85	222
321	2.13	236
402	1.54	228
452	1.13	231
∞	1.87	

Mean 0.00226

$\frac{N}{1}$ H_2SO_4, t=30°.

Time in minutes	α	K
0	12.98°	—
48	9.38	0.00504
82	7.35	499
100	6.30	508
129	4.91	509
168	3.40	518
207	2.04	511
260	0.63	538
300	−0.22	517
379	−1.47	523
∞	−3.77	—

Mean 0.00514

$\frac{N}{1}$ H_2SO_4, t=35°.

Time in minutes	α	K
0	6.68°	
21	4.98	0.0104
41	3.78	099
59	2.53	110
75	2.20	098
103	1.43	090
143	0.43	089
183	−0.45	094
253	−0.99	085
∞	−2.00	

Mean 0.0096

$\frac{N}{1}H_2SO_4+\frac{N}{10}Fe_2(SO_4)_3$, t=25°.

Time in minutes	α	K′
	6.68°	
59	5.58	0.00233
86	5.23	216
118	4.48	252
145	4.21	235
185	3.78	224
235	3.20	222
305	2.10	251
385	1.36	253
435	1.08	244
∞	−1.87	

Mean 0.00237

20 % Sucrose, $\frac{N}{1}$ H_2SO_4 + $\frac{3N}{10}$ $FeSO_4$, t=25°.

Time in minutes	α	K′
0	12.78	
58	11.36	0.00153
123	9.53	146
156	8.83	174
243	6.88	179
306	6.01	170
363	4.83	178
453	4.38	154
573	1.91	183
∞	−3.92	

Mean 0.00167

$\frac{N}{1}H_2SO_4+\frac{N}{50}$ $FeSO_4$,

Time in minutes	α	K′
	6.78	
25	5.68	0.00544
51	4.96	467
83	3.88	491
114	3.03	516
152	1.71	580
203	1.36	485
240	0.76	496
∞	−1.87	

Mean 0.00511

$\frac{N}{1}H_2SO_4+\frac{N}{25}$ $FeSO_4$, t=30°.

Time in minutes	α	K′
	6.39	
22	5.63	0.00441
49	5.02	372
82	3.86	492
112	3.03	469
152	1.86	527
202	1.40	463
239	0.78	481
∞	−1.82	

Mean 0.00464

$\frac{N}{1}H_2SO_4+\frac{N}{2}FeSO_4$,

Time in minutes	α	K′
	7.18	
15	6.63	0.00406
46	5.75	363
71	4.88	400
89	4.63	360
132	3.75	348
173	2.76	372
271	1.26	373
331	0.42	392
388	0.13	365
∞	−2.12	

Mean 0.00375

$\frac{N}{1}H_2SO_4+\frac{N}{1}FeSO_4$, t=30°.

Time in minutes	α	K′
	6.96	
39	5.70	0.00394
70	4.88	383
89	4.40	384
126	3.78	354
173	2.88	350
223	1.88	384
276	1.38	363
332	1.03	335
388	0.88	300
∞	−0.187	

Mean 0.00361

$\frac{N}{1}H_2SO_4+\frac{N}{25}CuSO_4$, t=30°.

Time in minutes	α	K′
	6.73	
32	5.43	0.00515
45	4.98	508
80	3.93	495
101	3.18	531
185	1.58	497
245	0.62	511
287	0.02	535
358	−0.37	495
∞	−1.82	

Mean 0.00511

$\frac{N}{1}H_2SO_4+\frac{N}{50}Fe_2(SO_4)_3$, t=30°.

Time in minutes	α	K′
	13.13	
71	8.13	0.00500
111	5.63	536
164	3.40	532
215	1.85	523
269	0.32	541
329	−0.49	513
391	−1.49	532
∞	−3.57	

Mean 0.00525

$\frac{N}{1}H_2SO_4+\frac{N}{25}Fe_2(SO_4)_3$, t=30°.

Time in minutes	α	K′
	6.63	
37	5.13	0.00542
70	3.90	573
112	2.62	594
165	1.31	627
215	0.71	587
269	0.13	576
329	−0.37	573
∞	−1.62	

Mean 0.00582

$\frac{N}{1}H_2SO_4+\frac{N}{25}Fe_2(SO_4)_3$, t=30°.

Time in minutes	α	K′
	6.73	
33	5.28	0.00567
45	5.02	499
80	3.95	495
100	3.38	496
155	2.01	523
185	1.61	499
245	0.38	562
286	0.23	507
358	−0.23	478
∞	−1.76	

Mean 0.00514

$\frac{N}{1}H_2SO_4+\frac{N}{25}Al_2(SO_4)_3$, t=30°.

Time in minutes	α	K′
	6.76	
47	5.13	0.00451
81	4.18	444
100	3.56	470
128	2.78	490
168	2.18	458
206	1.51	442
258	0.88	453
298	0.15	500
381	−0.27	456
∞	−1.77	

Mean 0.00463

$\frac{N}{1}H_2SO_4+\frac{3N}{10}FeSO_4$, t=35°.

Time in minutes	α	K′
	6.68	
24	5.51	0.00613
48	4.40	646
68	3.48	689
109	2.13	696
150	1.61	599
218	0.13	666
277	−0.42	640
∞	−1.87	

Mean 0.00650

20 % Sucrose, $\frac{N}{1}H_2SO_4+\frac{N}{10}Fe_2(SO_4)_3$, t=35°.

Time in minutes	α	K′
	6.68	
14	5.53	0.0104
33	3.88	122
54	3.28	95
94	1.61	97
135	0.38	100
203	−0.79	105
264	1.78	
66		
		Mean 0.0104

In the following table, the first column gives the concentration of the salt, the second the velocity constant (K′) and the third the ratio $\left(\frac{K'}{K}\right)$ of the velocity constant to that (K) obtained in the absence of salt.

t=25°.

	K′	$\frac{K'}{K}$
$\frac{N}{10}$ $Fe_2(SO_4)_3$	0.00237	1.049
$\frac{3N}{10}$ $FeSO_4$	0.00167	0.739

t=30°.

$FeSO_4$	K′	$\frac{K'}{K}$
N/50	0.00511	0.994
N/25	0.00464	0.903
N/2	0.00375	0.730
N/1	0.00361	0.702
$Fe_2(SO_4)_3$		
N/50	0.00525	1.021
N/25	0.00582	1.132
N/25 K_2SO_4	0.00514	1.000
„ $Al_2(SO_4)_3$	0.00463	0.901
„ $CuSO_4$	0.00511	0.994

$t=35°$.

	K′	$\frac{K'}{K}$
$\frac{N}{10}Fe_2SO_{43}$	0.0104	1.083
$\frac{3N}{10}Fe(SO_4)$	0.0065	0.677

The temperature coefficient of the velocity constant $\frac{K_{35}}{K_{25}}$ was found by calculation to be 4.4, 3.9 and 4.2 in the sulphuric acid, $H_2SO_4+FeSO_4$, and $H_2SO_4+Fe_2(SO_4)_3$ solutions respectively.

The velocity of the reaction with sulphuric acid is accelarated by the presence of ferric sulphate within the experimental conditions, but the ferrous salt retards, and the presence of potassium and cupric salts has no effect on, the velocity constant. These facts can not be explained by attributing the phenomena to the change in the degree of ionization of the acid caused by the salts or by "monohydrol" (H_2O) occurring in the solvent.[1]

July 1931

Laboratory of Organic & Bio-Chemistry.

1. L. E. Bowe: Jour Phy. Chem., **31**, 291 (1927).

Studies on Sesquiterpenes, II
Sesquiterpene and Sesquiterpene Alcohol from Japanese Cedar Oil (Cryptomeria Japonica or Sugi Oil)

By

Sakujiro Kimura and **Susumu Mizoshita**

(Received September 14, 1931)

It is said in Japan that *sake* is usually preserved in a Japanese cedar wood tank in order to flavour the liquor with an essential oil that occurs naturally in the wood. Chemical studies of the essential oil have been made by many investigators; sesquiterpenes and sesquiterpene alcohols from the root and the trunk have been studied by T. Kimoto[1], S. Keimatsu[2] and H. Kimura[3], and S. Uchida[4] has reported on some sesquiterpene and alcohol isolated from leaves. The results of these researches are shown in the following table.

Researcher			B. p.	d	n_D	$[\alpha]_D$
T. Kimoto	Sugiol	$C_{20}H_{44}O$	264	0.935	—	—
S. Keimatsu	Cryptene	$C_{15}H_{24}$	267	0.925	—	+18.6
H. Kimura		$C_{15}H_{24}$	$(150-160)_{17}$	—	—	—
		$C_{15}H_{24}$	$(150-160)_{17}$	0.918	—	−10.3
	Cryptomeriol	$C_{15}H_{25}OH$	$(162-163)_{10}$	0.964	—	−37.5
S. Uchida		$C_{15}H_{24}$	266–268	0.934	1.5041	+15.2
		$C_{15}H_{24}$	262–275	—	—	—
		$C_{15}H_{26}O$	284–286	0.962	1.5048	+16.8

Although many investigations of the chemistry of the sesquiterpene and sesquiterpene alcohol obtained from Japanese cedar oil have been

1. Complete Abstracts of Japanese Chemical Literatures, Series I, Vol. II, 62 (Japanese)
2. Ibid., 226.
3. Ber. Deutsch. Pharm. Ges., **19**, 369 (1909).
4. J. A. C. S., **38**, 687 (1916).

carried out from different points of view, little definite information has been given about them beyond their chemical formula. The writers have therefore undertaken the present investigation of Japanese cedar oil which came to their hands through the courtesy of Dr. T. Kainosho, Director of the Takasago Perfumery Company near Tokyo, and which was prepared by steam distillation from cedar roots grown at Tosa.

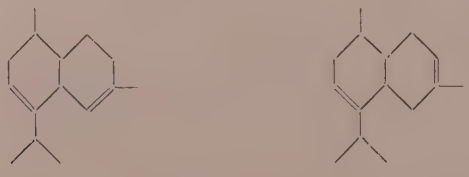
The essential oil used in this research was a bluish green viscous liquid and showed the following physical constants: B. p. $=(255-285)_{754mm}$; $d_4^{25}=0.936$; $n_D^{25}=1.508$; $[\alpha]_D=-16.7$; acid val. $=0.9$; ester val. $=8.9$.

The separation of hydrocarbon and alcohol from the oil was performed by means of sodamide and the yield was 54 % hydrocarbon and 38 % alcohol. The crude sesquiterpene, thus obtained, was a pale yellow liquid, boiling at $(140-155)_{17mm}$, $d_4^{25}=0.922$; $n_D^{25}=1.515$; $[\alpha]_D=-20°$. It was distilled in vacuo to isolate a hydrocarbon of definite composition, and a colourless liquid of the composition $C_{15}H_{24}$ was obtained, which, showing the physical constants; B.p. $=(108-114)_{4.5mm}$; $d_4^{25}=0.9150$; $n_D^{25}=1.5085$; $[\alpha]_D=-22.4$; M.R. $=66.4$ (theory $C_{15}H_{21}F_2=66.1$), was assumed from its physical properties to contain two double bonds in the molecule.

This hydrocarbon named *kiganene* by the writers resembles in its properties that of the sesquiterpene $C_{15}H_{24}$ B.p. $=(150-160)_{17mm}$ obtained previously by H. Kimura but differs from that studied by other investigators.

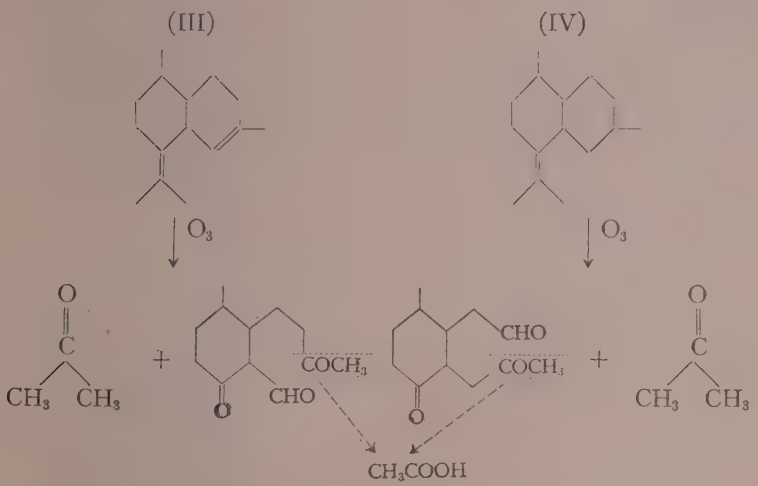
It forms with hydrogen chloride cadinene dihydrochloride[1] and cadalene by catalytic oxidation at high temperature in the presence of palladium asbestos[2]. These facts indicate that the kiganene is a bicyclic compound having the same carbon skeleton as the cadinene molecule and can be represented by one of the two formulae

(I) (II)



1. F. W. Semmler: Die Aetherischen Oele, II, 561.
2. S. Kimura: These memoirs, A, **14**, 186 (1931).

When, however, kiganene was oxidized with ozone, acetone and acetic acid were formed, and the reaction for their formation can be explained in the following manner by taking formula (III) or (IV) as its structure.



The structural formula for kiganene and the position of the double bonds in the molecule will be discussed later when the structure of the sesquiterpene alcohol occurring in the essential oil with the hydrocarbon has been decided, the two compounds being assumed to be intimately connected biochemically.

A crude sesquiterpene alcohol was separated from the hydrocarbon as a sodium compound by treating the oil with sodamide, showing the constants, $d_4^{25}=0.953$; $n_D^{25}=1.503$; $[\alpha]_D=-19°$. It was purified by repeated vacuum distillation, and a very viscous yellowish liquid of the constants B. p.$=(145-150)_{9mm}$; $d_4^{25}=0.9657$; $n_D^{25}=1.5055$; $[\alpha]_D=-6.34$; M. R.$=68.2$ was isolated. From these properties and the analytical figures (C$=80.8$; H$=11.4$; O$=7.8$) we learned that the fraction consisted of alcohol $C_{15}H_{26}O$ with one double bond in the molecule ($C_{15}H_{26}OF_1=68.1$). It changes in colour, on being kept in a bottle, to bluish green.

These properties of the alcohol so far studied, resemble those of the cryptomeriol isolated from the cedar root and studied by H. Kimura and also of the sesquiterpene alcohol obtained from cedar leaves by S. Uchida, and therefore the alcohol was called *kiganole*.

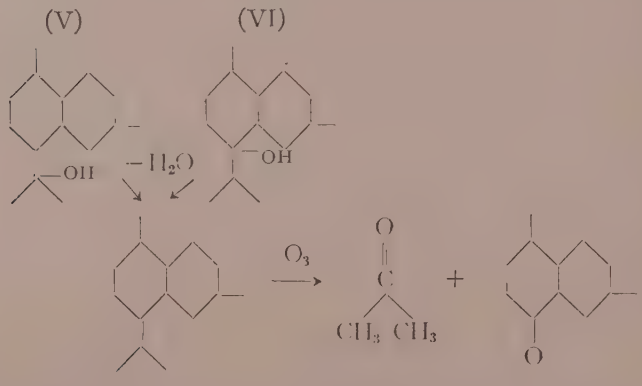
When kiganole was subjected to oxidation by the Vesterberg method[1], cadalene was formed, and a hydrocarbon $C_{15}H_{24}$, B. p. = $(115-146)_{6mm}$; $d_4^{25}=0.928$; $n_D^{25}=1.508$; $[\alpha]_D=-15°$, resulted on heating with phthalic anhydride; it probably has two double bonds in its molecule.

On reduction, kiganole gave a saturated alcohol (dihydrokiganole) $C_{17}H_{28}O$, B. p. $=(124-128)_{4.5mm}$; $d_4^{25}=0.9547$; $n_D^{25}=1.4964$; $[\alpha]_D=-3°$, which on being treated with acetic anhydride without formation of any ester, yielded an unsaturated hydrocarbon $C_{15}H_{26}$, B.p. $=(102-108)_{4.5mm}$; $d_4^{25}=0.8999$; $n_D^{25}=1.4932$; $[\alpha]_D=+2°$, this hydrocarbon gives rise to acetone on oxidation with ozone.

These facts favour the view that the dihydrosesquiterpene alcohol is a tertiary alcohol represented by either formula V or VI, and the unsaturated hydrocarbon formed by dehydration has the double bond between 4 and 8 carbon atoms. The saturated sesquiterpene alcohol formed by reduction of kiganole is, therefore, isomeric with the alcohol prepared by the hydrogenation of the sesquiterpene alcohol from camphor blue oil.

Dihydrosesquiterpene alcohol derived from kiganole of the Japanese cedar oil.	Dihydrosesquiterpene alcohol derived from the sesquiterpene alcohol of camphor blue oil.
B. p. $(124-128)_{4.5mm}$.	$(145-150)_{12mm}$.
d_4^{25} 0.9547	0.9388
n_D^{25} 1.4964	1.4901

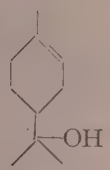
The properties of these compounds, as will be seen in the table,



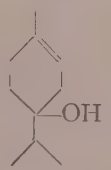
1. Ber., **36**, 4260 (1903); L. Ruzicka und J. Meyer: Helv., **4**, 505 (1921).

will be different from each other, and are in agreement with structure V for our compound and VI for the isomer[1].

This opinion as to the structure of the sesquiterpene alcohols is based on the fact that the physical constants of monoterpene alcohols have a close connection with the position of the hydroxyl group in their molecule; i. e. α-terpineol[2] in which hydroxyl group is joined to carbon 8 shows higher values in its physical constants than terpinenol-4[2].



α-Terpineol

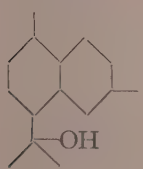


Terpinenol-4

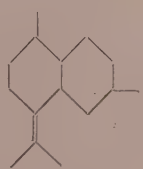
B. p.	217—218	209—212
d	0.940^{15}	0.9265^{19}
n_D	1.4808^{20}	1.4785^{19}

If such a relation between the physical constants and the position of the OH group of monoterpene alcohols holds in the case of sesquiterpene alcohols, dihydrokiganole which shows higher physical constants than the isomer obtained from camphor oil, should have formula V for its structure. If we accept the structural formula V for

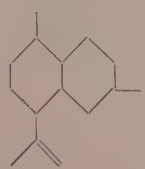
(V)

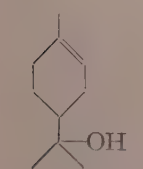


(VII)



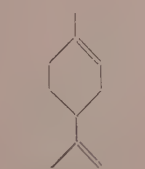
(VIII)





α-Terpineol

Terpinolene



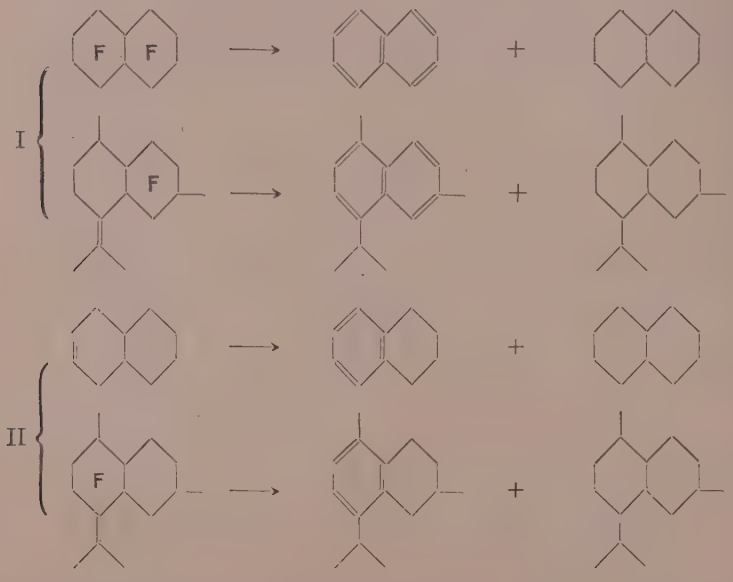
Limonene

1. S. Komatsu, H. Fujimoto and S. Tanaka: These Memoirs, A, **14**, 149 (1931).
2. E. Gildemeister: Die Aetherischen Oele, Band I, 394, 400.

dihydrokiganole, the structure for the hydrocarbon $C_{15}H_{26}$ formed by dehydration of the alcohol should be represented by either formula VII or VIII, and the chemical relation between these two compounds is obviously alike to that in the formation of limonene and terpinolene from *α*-terpineol by dehydration as shown by Wallach[1].

The fact that the unsaturated hydrocarbon derived from dihydrokiganole yields acetone on oxidation with ozone disposes of the formula VII for this compound.

In order to determine the position of the hydroxyl group and the double bond in the molecule of kiganole the writers have applied the method of catalytic oxidation-reduction in the presence of palladium to the unsaturated hydrocarbon $C_{15}H_{24}$ generated from kiganole by dehydration, the process which has already been used by one of the writers (S. Kimura) in the investigation of hydronaphthalenes[2] for the determination of their chemical structure. It has been confirmed that a hydronaphthalene having the double bond in each hexamethylene ring yields naphthalene and decahydronaphthalene on oxidation-reduction, while from hydrocarbons, in which two double bonds occur in the



1. Ann., **275**, 103 (1893); **291**, 361 (1896).
2. Loc. cit.

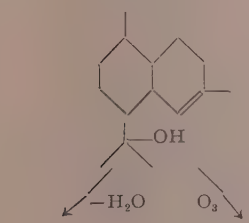
same ring, tetrahydro- and decahydronaphthalenes have actually been produced.

As a matter of fact, the hydrocarbon $C_{15}H_{24}$ obtained from kiganole $C_{15}H_{26}O$ catalytic oxidation-reduction at 320° in the presence of palladium asbestos, yielded cadalene and decahydrocadalene, and the reaction should be represented by scheme I but not by II; consequently, the two double bonds of the hydrocarbon occur in different rings.

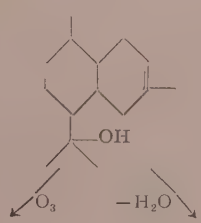
	$C_{15}H_{24}$	→	$C_{15}H_{18}$	+	$C_{15}H_{28}$
B. p.	$(108-114)_{4.5mm}$		$(118-125)_{4.5mm}$		$(96-99)_{4.5mm}$
d_4^{25}	0.9138		0.921		0.8840
n_D^{25}	1.5058		1.523		1.4800

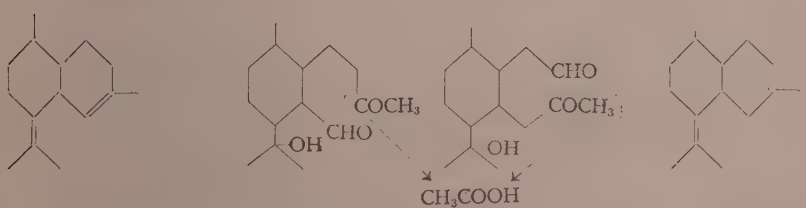
Furthermore, the fact that oxidation of the sesquiterpene alcohol with ozone gives acetic acid as one of the reaction products is explained by applying as its structure formula IX or X.

(IX)



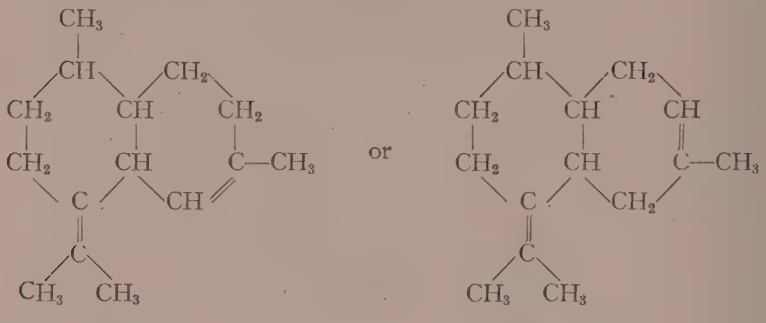
(X)





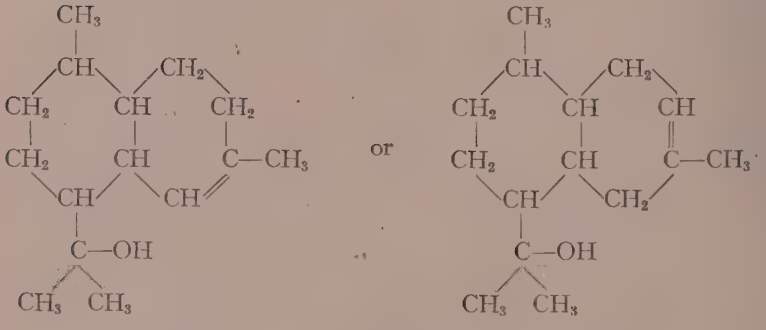
Accordingly, for the sesquiterpene kiganene occurring with the sesquiterpene alcohol kiganole of formula IX or X in cedar oil, either structure III or IV should be proposed and this proposition for the

structure is clearly endorsed by the hypothesis put forward by Prof. S. Komatsu and his collaborateurs[1] in their study of the sesquiterpene and alcohol obtained from camphor oil, that the chemical structure of terpene hydrocarbons shows a close relationship to that of the terpene alcohols which occur side by side in the same essential oil.



(III) or (IV)

Kiganene



(IX) or (X)

Kiganole

Experimental

The essential oil used in this experiment was prepared by steam distillation from the roots of Japanese cedars grown at Tosa. It is a

1. Loc. cit.

viscous yellowish green liquid, B. p.$=(255-285)_{764mm}$; $d_4^{25}=0.936$; $n_D^{25}=1.508$; $[\alpha]_D=-16.7$; acid val.$=0.9$; ester val.$=8.9$.

For the separation of hydrocarbon from alcohol, 2810 gms. of the oil were heated with sodamide on a water bath under reduced pressure until no more ammonia gas was evolved. After the hydrocarbon had been distilled under diminished pressure, the free alcohol was isolated from alcoholate by decomposition with water. The yield of crude sesquiterpene and crude sesquiterpene alcohol was 1528 gms. (54 %) and 1060 gms. (38 %) respectively with 172 gms. (6 %) of tarry matter, and the physical constants were ($d_4^{25}=0.922$; $n_D^{25}=1.515$; $[\alpha]_D=-20.1$) for the hydrocarbon and ($d_4^{25}=0.953$; $n_D^{25}=1.503$; $[\alpha]_D=-19.5$) for the alcohol.

I. Kiganene $C_{15}H_{24}$

(A) Cadinene dihydrochloride

When dry hydrogen chloride gas was passed into the crude sesquiterpene, cadinene dihydrochloride M. p.$=117-118°$[1] was formed with a yield of about 60 %.

(B) Purification of Sesquiterpene

80 gms. of crude sesquiterpene containing 60 % cadinene hydrochloride yielding compound were purified by distillation with metallic sodium under 4.5 mm. pressures.

	Fraction	Yield (gms.)	d_4^{25}	n_D^{25}	$[\alpha]_D$	M.R.
(1)	108—114°	47	0.9150	1.5085	−22.4	66.4
(2)	114—118°	17	0.9315	1.5119	—	—

Fraction (1) which formed the main portion of the essential oil was a colourless liquid turning to a yellowish brown colour gradually on standing in the air, and was assumed to be composed of a bicylic sesquiterpene by reference to its physical constants (M. R. calculated for $C_{15}H_{21}F_2$ is 66.1), and named *kiganene*.

1. F. W. Semmler: Die Aetherischen Oele, II, 561.

(C) Oxidation of Kiganene with Ozone

Ozonized oxygen was passed into a solution of 4 gms. of kiganene in 40 c.c. of carbon tetrachloride, and some iodoform was found in a potassium iodide solution placed after the reaction tube.

The ozonide, separated from carbon tetrachloride solution, was decomposed with water, and the aqueous solution separated from oily matter gave a blood-red colour with ferric chloride and sodium carbonate and also mercurous acetate with mercurous nitrate[1], due to the presence of acetic acid in the solution, but no reaction for formaldehyde and formic acid was noticed with the aqueous solution.

II. Kiganole $C_{15}H_{25}O$

(A) Purification of Sesquiterpene Alcohol

587 gms. of crude sesquiterpene alcohol separated from sesquiterpene by means of sodamide were fractionated under 9 mm. pressure into the following fractions :—

	Fraction	Yield gms.	d_4^{25}	n_D^{25}	$[\alpha]_D$	M.R.
(1)	122–132°	61	0.9399	1.5074	−14.04	—
(2)	132–142	24	0.9462	1.5061	−21.56	—
(3)	142–145	120	0.9523	1.5050	−11.0	—
(4)	145–150	212	0.9657	1.5055	− 6.34	68.2
(5)	150–167	21	0.9750	1.5132	—	—

Fractions (1), (2) and (3) were assumed from their physical constants to be composed mostly of hydrocarbon. Fraction (4) which was a viscous, yellowish green liquid changed its colour to bluish green gradually on standing in air. The physical constants and the analytical results indicate that this fraction consists of a bicyclic sesquiterpene alcohol of M. R. $C_{15}H_{25}OF_1 = 68.1$ and named *kiganole*. The analytical results are as follows: 0.1490 gm. subst., gave 0.4415 gm. CO_2 and 0.1534 gm. H_2O. Found: C = 80.8; H = 11.4; requires C = 81.1; H = 11.7 for $C_{15}H_{26}O$.

1. L. Rosenthaler: Der Nachweis Organischer Verbindungen, 284, 285.

(B) Dehydrogenation of Kiganole with Sulphur

10 gms. of kiganole were heated with 5 gms. of sulphur at 150—180°C for about 10 hours and the reaction product was distilled under reduced pressure, and then on metallic sodium, and 1.7 gms. of hydrocarbon of the following physical constants were obtained: B.p.=$(172-175)_{21mm}$; $d_4^{25}=0.9667$; $n_D^{25}=1.5785$. It yielded cadalene picrate[1] melting at 114—115°.

(C) Reaction of Kiganole with Phthalic Anhydride

10 gms. of kiganole were heated with an equal weight of phthalic anhydride at 120° for about 8 hours and the hydrocarbon formed by the reaction gave the following constants: B.p.=$(115-146)_{6mm}$; $d_4^{25}=0.928$; $n_D^{25}=1.508$; $[\alpha]_D=-15.1$.

(D) Catalytic Reduction of Kiganole

(a) The Reduction of Kiganole by colloidal Palladium and Hydrogen[2]

5 gms. of the alcohol were dissolved in 25 gms. of glacial acetic acid and reduced with hydrogen of 1.6 atmospheric pressures in the presence of colloidal palladium. The absorption of hydrogen gas was about 85 % of the theoretical value to saturate one double bond in the molecule. Thus, 54 gms. of kiganole yielded 46.1 gms. of the hydrogenated compound, B.p.=$(115-130)_{4.5mm}$; $d_4^{25}=0.945$; $n_D^{25}=1.495$; $[\alpha]_D=-5.4$, which were fractionated under 4.5mm. pressures into the following 3 portions.

	Fraction	Yield gms.	d_4^{25}	n_D^{25}	$[\alpha]_D$	M.R.
(1)	107—124	16.6	0.9316	1.4928	−13.0	—
(2)	124—128	16.4	0.9547	1.4964	− 3.2	68.7
(3)	128—134	5.4	—	—	—	—

Fraction (1) was assumed from its physical constants to be composed of hydrocarbon formed by dehydration of the alcohol, and fraction

1. L. Ruzicka u. J. Meyer: Helv., **4**, 508 (1921).
2. Skita: Ber., **45**, 3589 (1912).

(3) was the unchanged kiganole. Fraction (2) was a colourless viscous liquid and was supposed from the physical constants and analytical results to consist of dihydrokiganole $C_{15}H_{28}O$ (theory for M.R.=68.6).

On analysis 0.1618 gm. of subst., gave 0.4769 gm. CO_2 and 0.1760 gm. H_2O. Found: C=80.4; H=12.1; requires C=80.4; H=12.5 for $C_{15}H_{28}O$.

(b) Catalytic Reduction under High Pressure and Temperature

46 gms. of kiganole were reduced in the presence of reduced nickel at 140° under 70 atmospheric pressures of hydrogen, and the absorption of hydrogen was 25.9 atmospheric pressures, whereas the theoretical value of hydrogen for the saturation of one double bond corresponds to 23.2 atmospheric pressures. The reaction product ($d_4^{25}=0.941$; $n_D^{25}=1.493$) was fractionated under 4.5 mm. pressures into the following 3 portions.

	Fraction	Yield gms.	d_4^{25}	n_D^{25}	$[\alpha]_D$
(1)	112—125	13	0.9209	1.4922	+2.04
(2)	125—129	25	0.9492	1.4940	+7.07
(3)	129—135	3	—	1.4982	—

The physical constants indicate that fraction (3) consists of dihydrokiganole $C_{15}H_{28}O$.

(E) Dehydration of the Dihydrokiganole $C_{15}H_{28}O$

12 gms. of the dihydrokiganole obtained by reduction in the presence of colloidal palladium were heated in a sealed tube with an equal weight of acetic anhydride at 150° for about 5 hours, the reaction product being distilled under diminished pressure with metallic sodium after being separated from the acid, and 8.6 gms. of hydrocarbon were obtained. It showed the constants: B.p.=$(102\text{-}108)_{4mm}$; $d_4^{25}=0.8999$; $n_D^{25}=1.4932$; $[\alpha]_D=+2.1$; M.R.=66.7 (theor. val. for $C_{15}H_{26}F_1=66.6$).

In the second experiment, 15 gms. of the dihydrokiganole prepared by catalytic reduction under high temperature and pressure were dehydrated in the same manner as in the former case, and 9.8 gms. of the hydrocarbon, B.p.=$(102-106)_{4mm}$, $d_4^{25}=0.8944$; $n_D^{25}=1.4915$; $[\alpha]_D=+8.27$; M.R.=66.4) were obtained.

The hydrocarbon $C_{15}H_{26}$, thus formed by dehydration of the dihydrokiganole, was oxidized with ozone in the usual way and the formation of acetone was recognised in the reaction product.

(F) Dehydration of Kiganole $C_{15}H_{26}O$

30 gms. of kiganole were heated in a sealed tube, with an equal weight of acetic anhydride at 150° for about 6 hours, and 18.4 gms. of hydrocarbon $C_{15}H_{24}$ of the following physical constants resulted: B.p.$=(108-114)_{4.5mm}$; $d_4^{25}=0.9138$; $n_D^{25}=1.5058$; $[\alpha]_D=+21.23$; M.R.$=$ 66.2 (theor. val. for $C_{15}H_{24}F_2=66.1$).

(G) Catalytic Oxidation-Reduction of Hydrocarbon $C_{15}H_{24}$

11 gms. of the hydrocarbon prepared by dehydration of kiganole mentioned in F were passed with dry carbon dioxide gas over palladium asbestos heated at 320° for about 2 hours, and 10.4 gms. of the reaction product ($d_4^{25}=0.908$; $n_D^{25}=1.511$) were fractionated under 5 mm. pressures into the following 3 portions.

	Fraction	Yield gms.	d_4^{25}	n_D^{25}
(1)	99—106	2.3	0.9002	1.5050
(2)	106—118	6.4	—	1.5110
(3)	118—125	1.2	0.9210	1.5225

Fraction (1) after being treated with conc. sulphuric acid to remove any unsaturated hydrocarbon was distilled under diminished pressure, and decahydrocadalene[1] was isolated, which was confirmed to be so by the constants: B.p.$=(96-99)_{4.5mm}$; $d_4^{25}=0.8840$; $n_D^{25}=1.4800$.

Fraction (3) should consist of cadalene which yields a picrate of M.p.$=112°$, the melting point not showing any depression when it was mixed with pure cadalene picrate.

(H) Oxidation of Kiganole $C_{15}H_{26}O$ with Ozone

4 gms. of the sesquiterpene alcohol were oxidized with ozone in the usual way, and acetic acid was noticed to occur in the reaction product but no trace of formaldehyde and formic acid.

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1. S. Kimura, Loc. cit.

In conclusion, the writers wish to express their hearty thanks to Prof. S. Komatsu for his kind guidance and valuable suggestions throughout this work and also to Dr. T. Kainosho, the Director of the Takasago Perfumery Co. for his generous gift of the valuable material, which has made this investigation possible.

May 1930.

Laboratory of Organic- & Bio-Chemistry.

Biochemical Studies on the Soya Bean, I
The Chemical Changes of the Protein during the Germination of the Soya Bean in Darkness

By

Wei Sun Tao and **Shigeru Komatsu**

(Received September 14, 1931)

As already mentioned by Palladin in his book[1], the chemical processes which take place in the constituents of seeds during germination differ according to the chemical nature of their reserved materials. One of the writers has already studied[2] this subject in the case of starchy seeds with rice germinated in darkness. The present study is concerned with soya bean seeds which are rich protein and also in fatty matter and are employed in the Orient as food material.

The investigations of various seedlings carried on by E. Schulze[3] from 1878 to 1907, which were concerned mostly with the isolation of amino acids and other nitrogenous matters in them have stimulated many chemists to turn their attention to the study of the structure of seed proteins and the chemical changes of proteins in the seeds during germination. T. G. Thompson's investigation of the Alaska pea[4], C. J. V. Pettibone and C. Kennedy's study of corn[5], and B. Sure and W. E. Tottingham's study of the pea[6] may be mentioned as important researches in the field of germination, especially that of the last-mentioned authors, who have emphasized that asparagine is accumulated in shoots of pea seedlings germinated in the dark.

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1. B. E. Linvingston, "Palladin's Plant Physiology," (1917) 175.
2. Bull. of Chem. Japan, **5**, 65, 87, 109 (1930).
3. Landw. Jahrb., **7**, 411 (1878); **9**, 689 (1880); Zeit. Physiol. Chem., **12**, 405, (1888); **22**, 435 (1896); **24**, 19 (1898); Landw. Versuchsstat., (1906) 237.
4. Jour. Amer. Chem. Soc., **37**, 230 (1915).
5. Jour. Biol. Chem., **26**, 519 (1916).
6. Ibid., **26**, 535 (1916).

In the case of soya beans, P. Molliex[1] has studied the nitrogenous constituents of the seedlings, and W. Adolph has analysed the soya bean sprouts sold in a Chinese market, but their studies contain no information with regard to the chemical changes of the seed proteins during the germination. The writers, therefore, have undertaken the present research to find the chemical changes of the proteins, the germination of the seeds taking place by release of the stored substances.

Experiment

The beans used in this experiment are called "Hokaido" beans. They were harvested in Korea in 1928, and were kept in our laboratory.

To get fresh and healthy seedlings, avoiding putrefying action by moulds, the seeds were moistened with distilled water and kept in an incubator at 30°C for 4 days; the seedlings, from 2 to 7 cm. long, thus formed, were used in the experiment.

For comparison soya bean seeds were ground into powder and analysed.

In the analysis of seeds and seedlings, the content of moisture, the total reducing sugar, the soluble and insoluble polysaccharides, cellulose, pentosan, the total nitrogen, the total fat and ash were determined, and the results are shown in the following table I.

1. *Moisture.* About 10 gms. of the sample were dried at 105°C. in an air bath to a constant weight, the loss of weight being designated as the moisture content.

2. *Water extract.* About 10 gms. of the sample were treated with hot water and (a) total reducing sugars were estimated by determining the reducing power of the solution and calculated as glucose on an ash- and moisture-free basis; (b) soluble polysaccharides were determined by hydrolysing the extract with a 3 % sulphuric acid solution on a water bath for 3 hours; it was then neutralized with sodium carbonate and filtered, and the reducing sugars in this filtrate were estimated by means of Fehling's solution and calculated as d-glucose on an ash- and moisture-free basis. The difference between the content of the reducing sugars in the solution after and before the hydrolysis was designated the soluble polysaccharide content.

1. Ann. Chim. anal., **19**, 217 (1914).

3. *Insoluble polysaccharides.* The residue from the water extract was hydrolysed with a 3 % sulphuric acid solution on a direct flame for 3 hours, and the content of reducing sugars in the solution was estimated in the usual way.

4. *Pentosans.* These were determined by transforming them into furfural.

5. *Cellulose.* The amount of cellulose was determined by the method of Cross and Bevan.

6. *Total fat.* The samples were treated with petroleum ether and the extract was designated fat.

7. *Total nitrogen and protein.* The total nitrogen of the samples was estimated by Kjeldahl's method, and the protein content in the samples was calculated by multiplying the total nitrogen content by 6.25.

8. *Total ash.* The samples were ignited carefully at a low temperature and then heated again at a higher temperature to a constant weight.

Table I

	Seeds		Seedlings		Gain or loss
Dry wt. of 100 grains.	18.3 gms.	in %	17.8 gms.	in %	−0.5
Moisture	—	10.9	—	74.6	+47.96
Ash	—	4.9	—	4.3	−0.13
Fat	3.99	21.8	2.94	16.5	−1.05
Cellulose	0.83	4.5	1.31	7.4	+0.48
Pentosan	0.91	5.0	1.08	6.1	+0.17
Red. sugar	0.02	0.1	0.45	2.4	+0.41
Sol. polysacch.	0.78	4.3	0.39	2.2	−0.39
Insol. polysacch.	1.41	7.7	2.22	12.5	+0.81
Total N.	1.24	6.8	1.16	6.5	−0.08
Protein	7.75	42.6	7.25	40.6	−0.50

From the results shown in this table, loss in weight occurs during the germination of soya bean seeds as in the case of rice seeds, and in this the fat and nitrogenous matter are mostly concerned.

The proteins in both seeds and seedlings were isolated after the powderd samples had been treated with chloroform, by extracting with water at room temperature for 1 hour, the process being repeated 3

times, then with 10 % NaCl solution, and then 0.2 % and 7% NaOH solutions, and the nitrogen content in each extract was determined with the following results:

Table II

		in Seeds	for Total N	in Seedlings	for Total N	Gain or loss
N	Water extract	0.866 gms.	72.0 %	0.894 gms.	77.4 %	+0.028gms.
	10% NaCl	0.089	7.7	0.050	4.9	−0.039
	0.2% NaOH	0.058	5.0	0.034	3.3	−0.024
	7% NaOH	0.084	7.3	0.032	3.0	−0.052
	Sum	1.097	92.0	1.010	88.6	−0.087
N	Residue	0.14	12	0.15	12	+0.01

In the seedlings, compared with the seeds, the nitrogen in the water extract increased but was decreased in the other extracts, and the conversion of some proteins in the seeds into soluble nitrogenous compounds proceeded during the process of germination. The chemical processes taking place in the plant tissues were studied more closely by examining the chemical nature of the nitrogenous matter in the aqueous extract, and Wasteney's method[1] was employed to separate the hydrolytic products (proteose, peptone etc.) of proteins in the water extracts after albumin and globulin had been separated by coagulation, the solution being made up to pH 6 by adding a few drops of 10% acetic acid. The results are shown in the following table:

Table III

	in Seeds	for T.N.	in Seedlings	for T.N.	Diff.
Water extract-N	0.866 gms.	72 %	0.894 gms.	77 %	+0.028
Globulin-N	0.656	54.0	0.572	52.0	−0.084
Albumin-N	0.025	2.0	0.020	1.7	−0.005
Meta protein-N	0.020	1.6	0.004	0.4	−0.016
Proteose-N	0.051	4.0	0.112	9.8	+0.061
Peptone-N	0.057	4.5	0.060	5.2	+0.003
Sub. peptone-N	0.010	0.8	0.075	6.6	+0.065
Polypeptid-N	0	0	0.041	3.6	+0.041

1. Jour. Biol. Chem., **62**, 1 (1924).

When the seeds germinated in the dark, some of the proteins, especially globulin, were converted by partial hydrolysis into simpler forms such as proteose and peptone, and one part would evidently be decomposed further into urea and ammonia, showing an actual increase in the proteose, sub-peptone and polypeptide fractions. The nitrogen distribution in both seeds and seedlings will give clearer information as to the proteolytic changes of the proteins. These were studied with the whole grains and with the water extract, the latter being divided into precipitate and filtrate by making the solution PH 6, and both were examined separately.

Each sample was boiled with 20 % HCl for 20 hrs. and amide-N, humin-N, monoamido-N and diamino N were determined.

Table IV

	100 Grains of Seeds			100 Grains of Seedlings		
	whole grain	Water extract		whole grain	Water extract	
		soluble part	ppt. at pH 6		soluble part	ppt. at pH 6
Amide-N	135 mg.	18mg.	120mg.	185(+50)mg.	106(+88)mg.	103mg.
Humin-N	64	30	28	30(−34)	14(−16)	42
Mono-amino-N	798	62	775	770(−28)	200(+138)	585
Diamino-N	246	20	175	200(−41)	32(+12)	147
Sum	1243	130	1098	1185	352	877

The difference in the nitrogen distribution between seeds and seedlings is especially marked in the soluble part of the water extract (shown in brackets in the table); i. e. in the seedlings as may be seen in the table, the nitrogen of the amide- and mono-amino-forms was immensely increased owing to the presence of an acidic amino acid, such as glutaminic and aspartic acid, which probably forms the main constituent of the proteose and subpeptone fractions of the water extract, and the process of the conversion of the proteins in the seeds by the germination, as a whole, is very similar to the action of superheated water on proteins[1].

1. These Memoirs, **10**, 163, 241, 249 (1927); Jour. of Japan Chem. Soc., **51**, 729 (1930).

One unusual feature of the germination of seeds when compared with the chemical action of superheated water on proteins is the liberation of urea from the proteins. The content of urea and ammonia in both the seeds and the seedlings was estimated with 10 gms. of the samples by extraction with 250 c.c. boiling water and cooling to 40°C; and ammonia was fixed with $\frac{N}{14}$ H_2SO_4 solution which was generated from the solution by adding $Na_2CO_3^1$. The result was calculated for 100 grains of the seedlings and was found to be 5 mg. ammonia and 1.5 mg. of urea, but no trace was obtained from the seeds.

April 1931.

Laboratory of Organic & Bio-Chemistry.

1. O. Folin, Zeitschr. f. Physiol. Chem., **37**, 161 (1902).

Biochemical Studies on the Soya Bean, II
Action of the Enzymes in Soya Bean Seedlings on Glycinin

By

Wei Sun Tao

(Received September 14, 1931)

In the first part of this article, the writer and S. Komatsu stated that the proteins in the soya bean are transformed partly into simpler nitrogenous compounds during the process of germination, which is evidently the result of the action of enzymes occurring in the seedlings. J. P. Street and E. M. Baily[1] mentioned in their study of soya beans that a protease of the peptoclastic type occurs in it, but no further information was given.

A. Wurtz and E. Bouchut[2] have observed an enzyme in the papaya, which acts on protein; Chittenden[3] and his collaboraters have been engaged for many years in the study of the propeolytic enzymes of vegetable origin, and the papain from papaya has been investigated by them with regard to its hydrolytic action on egg albumin, which it converts into albumoses and peptone.

Other proteolytic enzymes in plant organs have been studied by A. F. Blood[4] (the erepsin of the cabbage) and by H. Lundin[5] (some enzymes of malt). Urease has been observed by many investigators to occur in soya beans and especially in the germinated seeds, and according to N. Onodera[6] the activity of the urease of soya bean extract is decreased by dialysis, but increased in the presence of a co-enzyme.

1. Jour. Indus. and Engin. Chem., **7**, 853 (1915).
2. Compt. Rend. Acad. Sci., **89**, 425; **91**, 787.
3. Chittenden: Studies in physiological Chem., 160.
4. J. Biol. Chem., **8**, 215 (1910).
5. Bioch. Zs., **131**, 193 (1922).
6. Biochem. Jour., **32**, 290 (1915).

The chemical changes of the proteins in soya beans during germination will be explained by the study of the proteolytic action of enzymes isolated from the germinated seeds on the soya proteins. Glycinin from the seeds was, therefore, treated with a water extract of the seedlings, which was supposed to contain some proteolytic enzymes.

In the experiments, the extract was prepared from 50 soya bean seedlings, crushed to powder, treated with 500 c.c. of distilled water at room temperature for 3 hrs., and filtered. The following experiments were performed:

50 c.c. of the seedling extract, which contained 44 mg. of nitrogen, were put into an Erlenmeyer flask. To this were added 0.5 gm. of pure glycinin which was isolated by Dr. Hibino from soya beans, containing 85 mg. N, and dissolved in 10 c.c. of 1 % NaCl solution, 40 c.c. water and 10 c.c. toluene. The flask was then stoppered with cotton and incubated at 40°C. The pH of this mixture is 6.46.

For comparison, an Erlenmeyer flask containing 50 c.c. of the extract covered with toluene was incubated at 40°C. The pH of this solution is 6.4.

Both the sample from the seedlings and the control after having been incubated at 40°C for 24 hrs., 48 hrs., 72 hrs., and 96 hrs., were heated on a water bath for about 30 mins. and then filtered. The total nitrogen in the filtrates was determined by Kjeldahl's method, and the free amino-N by van Slyke's method; the proteose, peptone and polypeptide, and pH value were also determined, with the following results:—

Table I

1

The Extract and Glycinin

Time for digestion	24 hrs.	48 hrs.	72 hrs.	96 hrs.
Total volume	90 c.c.	88 c.c.	90 c.c.	89 c.c.
Total-N	40.1 mg.	40.5 mg.	47.3 mg.	51.9 mg.
Free amino-N	7.7 „	10.8 „	12.6 „	12.6 „
Proteose-N	8.6 „	7.7 „	8.5 „	10.1 „
Peptone & polypeptid-N	31.5 „	32.8 „	38.8 „	41.8 „
pH	6.2	6.2	5.8	5.8

II

The Extract

Time for digestion	24 hrs.	48 hrs.	72 hrs.	96 hrs.
Total volume	92 c.c.	90	90	90
Total-N	24.4 mg.	24.8 mg.	28.8 mg.	32.9 mg.
Free amino-N	6.1	6.5	8.2	9.0
Proteose-N	3.8	4.2	7.3	9.0
Peptone & polypeptid-N	20.6	20.6	21.5	23.9
pH	6.2	6.0	6.0	5.8

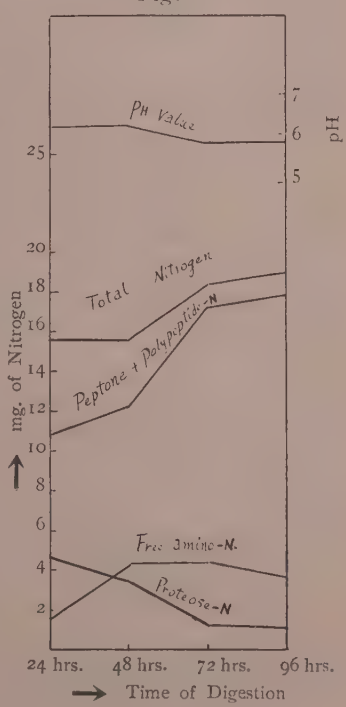
Table II.

Time for digestion	24 hrs.	48 hrs.	72 hrs.	96 hrs.
Total-N	15.7 mg.	15.7 mg.	18.5 mg.	19.0 mg.
Free amino-N	1.6	4.3	4.4	3.6
Proteose-N	4.8	3.5	1.2	1.1
Peptone & polypeptid-N	10.9	12.2	17.3	17.9

The chemical changes which actually occur in glycinin owing to the proteolytic enzymes in the extract are expressed by the results shown in Table II and Fig. 1, which were calculated from experimental results I and II in Table I.

The chemical mechanism for the conversion of glycinin by enzymes into simple nitrogenous compounds will be learned from the change in the nitrogen distribution of the reaction product with time. As a matter of fact, the nitrogen of the peptones and polypeptides increased and the proteose nitrogen decreased with progress of time, and the chemical changes of the protein is very like, as a whole, those of the nitrogenous matter in the soya bean during germination. The change in the free amino-N with time, as will be seen in the Fig. 1,

Fig. 1



which does not run parallel with that of the pH-value, is mostly due to the liberation of an acidic amino acid, such as aspartic or glutaminic acid, from the protein molecule in the course of digestion by the enzyme.

The enzymatic action of urease in seedlings is interesting in connection with the proteolytic action of other enzymes in them. 50 c.c. of the extract were, therefore, mixed with 5 c.c. of 1 % urea solution (23 mg. N), and kept for $1\frac{1}{2}$ hrs. at 40°C and the ammonia resulting from the enzymatic reaction was determined[1] by absorbing with $\frac{1}{14}$ N H_2SO_4 solution.

The experimental results show that 15.5 mg. N in urea were converted into ammonia in the seed extract, and 20.2 mg. N in the seedling extracts; in other words, the urease of the seedlings is more active on urea than that of the seeds.

In closing, the writer would like to offer her sincere thanks to Prof. S. Komatsu of Kyoto Imperial University for his kind guidance, to Prof. Nodzu and other members in her laboratory for their valuable advice and suggestions, and to Mr. T. Hibino for supplying her with the glycinin for these experiments.

July 1931.

Laboratory of Organic & Bio-Chemistry.

1. Zeit. f. Physiol. Chem., **37**, 161 (1902).

Catalytic Action at High Temperature and under High Pressure, V Catalytic Hydrogenation of Benzoic Acid

By

Shigeru Komatsu and **Keisaku Mitsui**

(Received September 14, 1931)

Catalytic hydrogenation of benzoic acid in the presence of reduced nickel was tried by Sabatier & Murat[1], by which process a trace of the acid was hydrogenated at 180°−200° into hexahydrobenzoic acid, and the process was regarded as inconvenient for this purpose. However, W. Ipatiew and O. Philipow[2] succeeded in converting benzoic acid into its hexahydro compound with a yield of 60 % of the theory by applying 100 atmospheric pressures of hydrogen and high temperature (300°) to its sodium salt in the presence of nickel oxide.

Subsequently the catalytic hydrogenation of aromatic carboxylic acids was usually performed by converting them into the sodium salt, and Professor Sabatier[3] has reported that the esters of benzoic acid are reduced more easily by his method than the free acid when the reaction is conducted at 180°, but that at higher temperatures the metal rapidly loses all its catalytic activity.

The report by R. Willstätter and D. Hatt[4] on the hydrogenation of benzoic acid with the aid of platinum, seems to us a very exceptional case, in which the reaction proceeded with great facility in glacial acetic acid solution.

An equimolecular mixture of benzoic acid (40 gms.) and ethyl alcohol (50 c.c.) was heated at 225° for 6 hrs. in an autoclave with 92

1. C. R., **154**, 924 (1912).
2. Ber. D. Chem. Ges., **41**, 1005 (1908).
3. C. R., **154**, 925 (1912)
4. Ber. D. Chem. Ges., **45**, 1477 (1912).

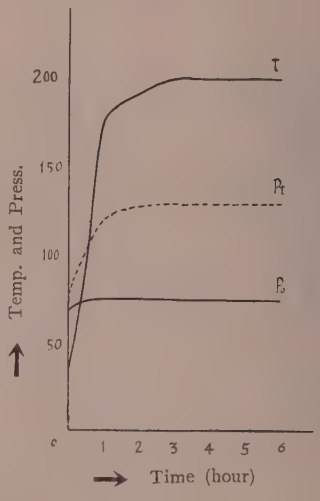
atmospheric pressures of hydrogen at 34° and 5 gms. reduced nickel. 29 gms. of reaction product separated from the catalyst showed $d_4^{25}=1.035$; $n_D^{25}=1.496$; acid value 11. (see Fig. I).

10 gms. of the product were treated with 5 % NaOH solution and 1.2 gms. of an oily substance insoluble in the alkali solution, showing B.p. 202°−222°; $d_4^{25}=1.034$; $n_D^{25}=1.494$, were fractionated.

	B. p.	Yield	d_4^{25}	n_D^{25}
1	203°−206°	11 %	1.017	1.487
2	206°−209°	73 %	1.033	1.495
3	residue & loss	16 %	—	—

Two fractions, (1) and (2), being mixtures of ethyl esters of benzoic and hexahydrobenzoic acids, were estimated separately for the proportion of these two components in them by means of their physical constants (ethyl benzoate B.p. 208°−209°; $d_4^{25}=1.0440$; $n_D^{25}=1.5015$; ethyl hexahydrobenzoate B.p. 190°−193°; $d_4^{25}=0.9524$; $n_D^{25}=1.4392$), and the amount of hexahydrobenzoate and benzoate in the reaction product was found by calculation to be 19 % and 78 % respectively.

Fig. 1



From the alkaline solution, 0.7 gm. of benzoic acid M.p. 122° was isolated, which corresponds to 3.3 % for the product.

In the second experiment, 20 gms. of benzoic acid, 25 c.c. of ethyl alcohol and 5 gms. reduced nickel were mixed in an autoclave and heated at 170°−205° for 5 hrs. under 78 atmospheric pressures of hydrogen at 31°, and 18.3 gms. of reaction product ($d_4^{25}=1.035$; $n_D^{25}=1.494$) were isolated; it was supposed to consist mostly of esters, the acid value of the product being 10.

5 gms. of the product contained 0.3 gm. of benzoic acid and 4.6 gms. of esters, and the latter was separated into two fractions by distillation and then the proportion of ethyl esters of benzoic acid and hexahydrobenzoic acid in them calculated.

	Fraction	Yield	d_4^{25}	n_D^{25}
1	201°–208°	3.1 gms.	1.028	1.491
2	208°–212°	1.5 „	1.039	1.498

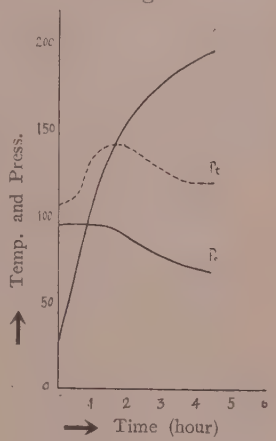
The results are ethyl benzoate 80 %, ethyl hexahydrobenzoate 12 % and benzoic acid 2 %.

The benzoic acid, as seen in these experiments, was partly hydrogenated and the two acids were almost entirely esterified, and the high yield of the esters (92 %) compared with that calculated from the esterification velocity of the acid by Menschutzkin[1], must be attributed either to the catalytic action of the reduced nickel or to the high pressure of hydrogen.

The small yield of hexahydrobenzoic acid ester by the reaction is due to the presence of free acid which acts as a negative catalyst, since the hydrogenation of benzoate runs very smoothly with quantitative yield of the hexahydro compounds.

50 gms. of ethyl benzoate B.p. 208–209°, $d_4^{25}=1.044°$, $n_D^{25}=1.5015$, were heated at 115° with 5 gms. reduced nickel under 100 atmospheric pressures at 25°, and the reduction was completed with absorption of 3 mols hydrogen as may be seen in the following Fig. 2.

Fig. 2



48.6 gms. of the product, $d_4^{25}=0.9614$; $n_D^{25}=1.4403$, were distilled and the fraction B.p. 185–193° consists of 90 % of the distillate which shows $d_4^{25}=0.953$; $n_D^{25}=1.439$ were composed of hexahydrobenzoate 87 % and benzoate 11 %.

The physical constants of the main fraction, 82 % of the product, were determined after it had been purified by distillation, and the fraction was found to consist of ethyl hexahydrobenzoate, B.p. 190°–193°; $d_4^{25}=0.9524$; $n_D^{25}=1.4392$.

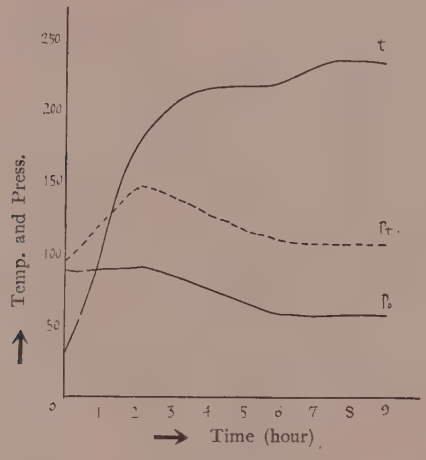
In the second experiment, 30 gms. ethyl benzoate were reduced at 190° under 100 atmospheric pressures of hydrogen at 26° in the presence of 5 gms. of reduced nickel. 3.3 mols of hydrogen were

1. Ann. **195**, 334; **197**, 193 (1879).

absorbed in $3\frac{1}{2}$ hours, and 30 gms. of the reaction product, $d_4^{25}=0.953$; $n_D^{25}=1.439$, were fractionated and the proportion of ethyl benzoate and ethyl hexahydrobenzoate was found by calculation in the usual way to be 7 % and 92 % respectively.

Hydrogenation of benzoic acid ethyl ester was tried in ethyl alcohol solution and it was confirmed that the solvent has no effect on the reaction. A mixture of 50 gms. of the ester, 50 c.c. of ethyl alcohol and 5 gms. reduced nickel was heated at 175 – 225° under 97 atmospheric pressures of hydrogen at 28°, and 3.3 mols hydrogen were absorbed in 4 hours by the reaction. (Fig. 3).

Fig. 3



51 gms. of the reaction product, $d_4^{25}=0.9303$; $n_D^{25}=1.432$, were fractionated with the following results:

	B. p.	Yield	d_4^{25}	n_D^{25}	Remark
1	–100°	30 gms.	–	–	Ethyl alcohol
2	100°–190°	0.9	0.882	1.436	
3	190°–196°	17.8	0.9541	1.441	Benzoate
4	196°–200°	0.6	0.9605	1.441	Hexahydrobenzoate
5	200°–	0.4	–	–	

The main fraction (3) was assumed from its physical constants to be composed of hexahydrobenzoate and benzoate and their proportion was found by calculation to be in the ratio of 9 : 1 ; the reaction product was assumed, therefore, to be composed of hexahydrobenzoate 95 % and benzoate 3 %.

Thus, benzoic acid was hydrogenated with quantitative yield by applying the high pressure and temperature method to its ethyl ester.

August 1931.

Laboratory of Organic & Bio-Chemistry.

Stereochemical Studies on Hydronaphthalenes, II*
Absorption Spectra of Hydronaphthalenes

By

Sakujiro Kimura

(Received September 16, 1931)

Our present knowledge concerning the chemical constitution and the arrangement of atoms in the molecule of naphthalene and its hydro compounds is mostly based on the studies of isomers, but no formula which satisfactorily explains the reactions of these compounds has yet been proposed. The problem of the stereochemistry of naphthalene, however, still remains to be studied further and may perhaps open up a new path to the end in view. The writer has therefore taken up this subject from the point of view of the ultra violet absorption spectra of naphthalene and its hydro compounds.

According to the investigations by Henri and others, benzene[1] shows seven absorption bands in the ultra violet region in its hexane solution, having a frequency interval of $\Delta\frac{1}{\lambda}=921\ \mathrm{cm}^{-1}$. This interval of the absorption bands $\left(\Delta\frac{1}{\lambda}=943\ \mathrm{cm}^{-1}\text{ and }1186\ \mathrm{cm}^{-1}\right)$ is also seen in the absorption bands of the methyl derivatives of benzene, such as toluene and p-xylene,[2] in which there is another group of absorption bands of a different frequency interval $\left(\Delta\frac{1}{\lambda}=236\ \mathrm{cm}^{-1}\text{ and }366\ \mathrm{cm}^{-1}\right)$. The first group of bands was attributed to the benzene nucleus and the origin of the absorption bands of the second group was regarded as connected with the methyl group in the molecule. Henri and his colaborateurs[3] studying the absorption spectrum of naphthalene, in a

* Part I, These Memoirs A, **14**, 173 (1931).

1. Henri: Etudes de Photochimie 128 (1919); Structure des molecules 108 (1925). Orndorff, Gibbs, McNulty and Shapiro: Jour. Am. Chem. Soc., **50**, 831 (1928).
2. Klingstedt: Compt. rend., **175**, 1065 (1922); Orndorff etc. loc. cit.
3. Henri and Laszlo: Proc. Roy. Soc., **105**, 662 (1924).

vapour state, have noticed that there are two series of absorption bands, the first one found in the 3200 Å—2820 Å region, consisting of more than 400 fine lines, is due to the naphthalene nucleus, and the second one composed of bands in the 2820 Å—2500 Å region is due to the activated molecule. Similar absorption spectra were shown by naphthalene in hexane solutions[1]; they also show two series of absorption bands and one band in the extreme ultra-violet at 2209A°, the one series composed of 9 bands a—k ($\lambda = 3200$Å—2930 Å)*, and the other of 8 bands 1—8 ($\lambda = 2881$ Å—2563 Å)*, and the first series classified into two groups, A and B, according to the frequency intervals $\Delta\frac{1}{\lambda}$ 1450 cm^{-1} and 450 cm^{-1}. Methylnaphthalene[2] in solution shows a series of absorption bands in the ultra violet region, which may be divided according to the frequency interval into three groups A $\left(\Delta\frac{1}{\lambda} = 1425\ cm^{-1}\right)$, B $\left(\Delta\frac{1}{\lambda} = 475\ cm^{-1}\right)$ and C $\left(\Delta\frac{1}{\lambda} = 328\ cm^{-1}\right)$, and the latter may be attributed to the presence of a methyl group combined with the naphthalene nucleus. In the following table, the frequency intervals of the absorption bands of benzene, naphthalene and their derivatives in solution are shown for reference.

	$\Delta\frac{1}{\lambda}$ (cm^{-1})		
	A	B	C
Benzene	921	—	—
Toluene	943	—	236
p-Xylene	1186	—	366
Naphthalene	1450	450	—
β-Methylnaphthalene	1425	475	328

The absorption spectrum of naphthalene was studied by the writer with its ethyl alcohol solution, which gives results similar to those obtained by Henri and Steiner[3] with the hexane solution but different from the results obtained by Baly and Tuck[4]. Two series of absorption

1. Henri et Steiner: Compt. rend., **175**, 421 (1922).
* See Table I in the experimental part.
2. Laszlo: Compt. rend., **180**, 205 (1925); Zeit. f. Phys. Chem., **118**, 371 (1925).
3. loc. cit.
4. Jour. Chem. Soc., **93**, 1902 (1908).

bands were found, one series composed of 9 sharp and intensive bands (A—K) in the ultra violet region ($\lambda=3400$ Å—2900 Å) which are divided into two groups according to the frequency interval (A) $\Delta\frac{1}{\lambda}=1480\ cm^{-1}$ and (B) $\Delta\frac{1}{\lambda}=540\ cm^{-1}$, and the other series composed of 5 broad and diffused bands in $\lambda=2900$ Å—2500 Å. The first series corresponds to the bands given by the naphthalene nucleus as mentioned by Henri, and the latter series corresponds to the bands which are said to originate from the activation of the molecule. When naphthalene is reduced to dihydro and tetrahydro compounds, the absorption spectra of their alcohol solutions, seen in the ultra violet region, are also composed of two series of absorption bands, the one series comprising two groups of the following frequency intervals, which are similar in value to those of naphthalene, but the spectra differ from that of naphthalene in the number of absorption bands.

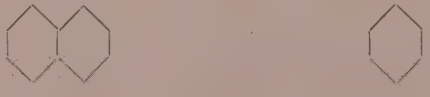
	$\Delta\frac{1}{\lambda}(cm^{-1})$	
	A	B
Naphthalene	1480	540
Δ^1-Dihydronaphthalene	1630	475
Tetrahydronaphthalene	1563	497

The absorption spectra shown by naphthalene solution are exhibited by solutions of the di- and tetra-hydronaphthalenes, but the absorption of light by benzene being different from that of its hydro compounds, 7 sharp absorption bands in the ultra violet region, due to the benzene nucleus, do not appear in the alcohol solutions of di- and tetra-hydrobenzenes. The relationship shown in the absorption spectra of these two series of compounds of naphthalene and benzene, leads to the idea that the chemical structure of benzene is different from that of its hydrogenated compounds, while di- and tetra-hydronaphthalene have the same chemical structure as naphthalene.

When the reduction of naphthalene was carried further to octahydronaphthalene and then to decahydronaphthalene, the absorption spectra of these two compounds in the ultra violet region were observed to be entirely different in nature from those of the other hydro compounds studied above, and to be composed only of broad diffused

bands in $\lambda = 2750$ Å—2400 Å, of frequency interval $\Delta\frac{1}{\lambda} = 1500\,\mathrm{cm}^{-1}$, which correspond to the second series of absorption bands of naphthalene, and the first series of the absorption bands due to the naphthalene nucleus was absent in these hydro compounds. These facts are in favour of the view that the chemical structure of the naphthalene molecule is partly changed in the octahydro- and decahydro-derivatives. The fact that the absorption spectra of the compounds of the naphthalene series are different from those of the benzene series may be explained by assuming a bicyclic structure for the naphthalene molecule; in the formation of dihydro- and tetrahydronaphthalene, the hydrogen atoms, may be added to one of the rings in the naphthalene molecule, but in the case of octahydro- and decahydronaphthalenes they are added to both rings. Accordingly, in the former case, the addition of hydrogen atoms to naphthalene does not effect its absorption spectra, while on further addition of hydrogen atoms only the second series of absorption bands will appear in the ultra violet region owing to the partial change in the chemical structure of naphthalene. The absorption bands of the second series, which are situated from the neighbourhood of $\frac{1}{\lambda} = 35000\,\mathrm{cm}^{-1}$ to the more ultra violet region as may be seen in Figs. 1—5, are observed to appear throughout all the compounds of the naphthalene series. As to the origin of these bands, the writer is inclined to accept the hypothesis that there is some vibration of a bicyclic carbon linking I, but hesitates to agree with the view proposed by Henri as described above, and some properties of benzene and its hydro compounds, which are not met with in naphthalene and its hydro compounds are explained by accepting the monocyclic carbon linking II for the compounds of the benzene series.

(I) (II)



Dr. Hagiwara's[1] observation made in the course of his study of terpenes, that pinane $C_{10}H_{18}$, the saturated bicyclic compound, exhibits a selective absorption band in the ultra violet region but that a saturated monocyclic hydrocarbon such as menthane $C_{10}H_{20}$ shows no selective absorption band, supports the writer's view that there is an absorption caused by the bicyclic ring.

1. Lectured at the meeting of Chem. Soc. Japan, March (1931).

If we assume that naphthalene is represented by a bicyclic structure, some vibration between the two rings, which arises round an axis connecting the carbon atoms 9 and 10, would cause broad diffused absorption bands of the second series. This opinion as to the absorption spectra of the bicyclic compounds, however, will be settled by future studies which will appear in an article in the near future from this laboratory.

The structural formula of naphthalene reported above from the study of absorption spectra, is similar in the form of the carbon skeleton to that proposed by Erlenmeyer[1] and Graebe[2] III but differs from the monocyclic formula IV advocated by Bamberger[3].

(III) (IV)

The writer's idea of the bicyclic nature of the naphthalene molecule is also confirmed by the study of the catalytic reduction of naphthalene and its derivatives under high temperature and high pressure[4]. When catalytic reduction of benzene under 80 atmospheric pressures of hydrogen was performed, the reaction began at 40° and proceeded very rapidly at 200°, and cyclohexane C_6H_{12} was produced as the reaction product, while naphthalene $C_{10}H_8$ absorbs hydrogen very slowly at 150° under 90 atmospheric pressures, and at 200° the yield of tetrahydronaphthalene $C_{10}H_8H_4$ was satisfactory; the latter compound was hydrogenated easily at 180° and under 90 atmospheric pressures of hydrogen to decahydronaphthalene $C_{10}H_8H_{10}$. These results lead the writer to the opinion that the distribution of energy in the naphthalene molecule differs from that of the benzene molecule in not being uniform, and this view of the distribution of energy in the naphthalene molecule was supposed from the fact that the absorption spectra of naphthalene and its hydro compounds due to the naphthalene nucleus are composed of two groups of bands of different frequency interval and this hypothesis was more clearly indicated in the experimental results obtained in the catalytic

1. Ann., **137**, 346 (1886).
2. Ber., **1**, 36 (1869).
3. Ann., **257**, 1 (1890).
4. Kagehira: Bull. Chem. Soc. Japan, **6**, 241 (1931).

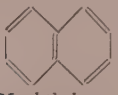
oxidation-reduction of hydronaphthalenes[1] carried out with dihydronaphthalene (I), tetrahydronaphthalene (II) and octahydronaphthalene (III). In those experiments it was proved that naphthalene and tetrahydronaphthalene, naphthalene and decahydronaphthalene, and tetrahydronaphthalene and decahydronaphthalene are formed from these compounds respectively, and the results shown in the following schemes are in favour of the view.

$$C_{10}H_8H_2 \longrightarrow C_{10}H_8 + C_{10}H_8H_4 \quad (I)$$
$$C_{10}H_8H_4 \longrightarrow C_{10}H_8 + C_{10}H_8H_{10} \quad (II)$$
$$C_{10}H_8H_8 \longrightarrow C_{10}H_8H_4 + C_{10}H_8H_{10} \quad (III)$$

The fact that dihydrobenzene and tetrahydrobenzene, on being subjected separately to this reaction, yield benzene and cyclohexane in each case, shows the uniformity of the distribution of energy in the benzene molecule. The reactions occurring in hydronaphthalenes can be easily explained by assuming that the hydrogen atoms 2H and 4H in di- and tetrahydronaphthalenes, being different in behavior from the 8H atoms in the octahydronaphthalene molecule, are distributed in the same ring while in the latter compound the 8 hydrogen atoms are shared between two rings, 6H to one, and 2H to the other.

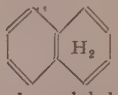
If the view as to the constitution of naphthalene advanced by Erlenmeyer and Graebe is extended to dihydro-, tetrahydro-, octahydro- and decahydronaphthalene, it is seen that these compounds are represented by formulae V—IX, of which formulae, V and IX are symmetrical in structure, while VI, VII, and VIII are unsymmetrical,

(V)



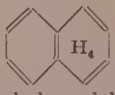
Naphthalene

(VI)



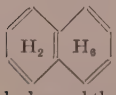
Dihydronaphthalene

(VII)



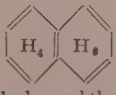
Tetrahydronaphthalene

(VIII)



Octahydronaphthalene

(IX)



Decahydronaphthalene

and in VIII, there occur asymmetrical carbon atoms 9 and 10, but it

1. Kimura: These Memoirs, A, **14**, 186 (1931).

loses its asymmetry when the reduction progresses to decahydronaphthalene.

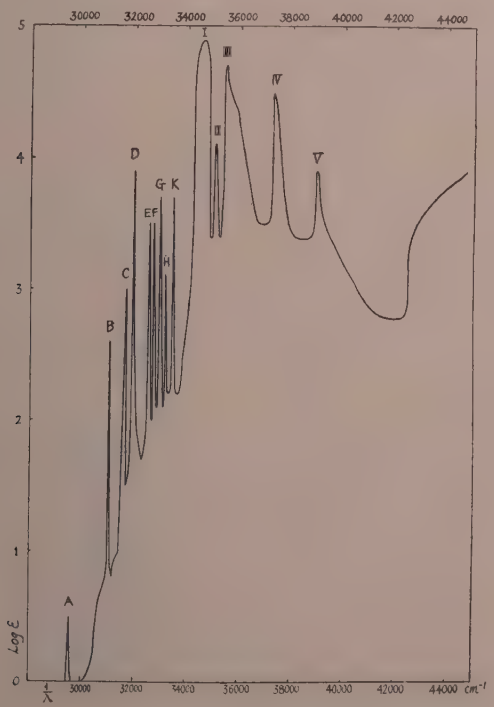
Experimental

In the experiments, the purified substances were dissolved in pure alcohol and light was passed from a Geissler hydrogen tube into the solution to get continuous ultra violet absorption spectra, which were photographed on Eastman's panchromatic film, with Hilger's spectrograph E_2. The value for $\log\varepsilon$ was calculated from the equation $J = J_0 . 10^{-\varepsilon cd}$: $\log\frac{J}{J_0} = -\varepsilon\, cd$, where J_0 and J = the intensity of light before and after being passed into a solution of thickness d cms. and concentration c; and the absorption curves were plotted, $\log\varepsilon$ and $\frac{1}{\lambda}$ cm^{-1} being taken as ordinate and axis respectively.

1. Naphthalene

Naphthalene was purified by distillation on Japanese acid clay and

Fig. 1



absorption spectra of its alcoholic solution were studied. The wave numbers of the absorption bands as shown in Fig. 1 and Table I, agree with the results obtained by Henri and Steiner[1] with hexane solutions. The absorption spectra of naphthalene solutions may be divided into two series. The first consists of sharp and distinct bands from A to K shown in Fig. 1, which are divided into groups A and B with the frequency intervals $\Delta\frac{1}{\lambda}=1450\ \mathrm{cm}^{-1}$ and $450\ \mathrm{cm}^{-1}$ respectively; band C is the most intense, the other bands being arranged A, B, F and H in ascending order of intensity. The second series is composed of 5 bands from I to V, broad and diffused. The bands of both series, as may be seen from following table, correspond to absorption bands a—k and 1—9 respectively of naphthalene hexane solution observed by Henri and Steiner.

Table I

Kimura			Henri and Steiner		
Band	λ(Å)	$\frac{1}{\lambda}(\mathrm{cm}^{-1})$	Band	λ(Å)	$\frac{1}{\lambda}(\mathrm{cm}^{-1})$
A	3384	29550	a	3207	31182
B	3219	31060	b	3148	31766
C	3160	31650	c	3110	32154
D	3126	31990	d	3067	32605
E	3071	32560	e	3040	32895
F	3059	32690	f	3010	33223
G	3031	32990	g	2994	33400
H	3019	33120	h	2975	33613
K	2992	33420	k	2930	34130
I	2888	34620	1	2881	34710
II	2856	35080	2	2852	35063
III	2825	35400	3	2835	35273
IV	2684	37250	4	2755	36297
V	2567	38950	5	2724	36711
			6	2650	37736
			7	2620	38168
			8	2563	39017
			9	2209	45269

1. Compt. rend., **175**, 421 (1922).

$$\left.\begin{aligned}
&\Delta\frac{1}{\lambda}(\text{B}-\text{A}) = 1510\ \text{cm}^{-1}\\
&\Delta\frac{1}{\lambda}(\text{E}-\text{B}) = 1500\ \text{,,}\\
&\Delta\frac{1}{\lambda}(\text{H}-\text{C}) = 1470\ \text{,,}\\
&\Delta\frac{1}{\lambda}(\text{K}-\text{D}) = 1430\ \text{,,}\\
&\Delta\frac{1}{\lambda}(\text{I}-\text{H}) = 1500\ \text{,,}
\end{aligned}\right\}\ \text{Mean. } \Delta\frac{1}{\lambda} = 1480\ \text{cm}^{-1}$$

$$\left.\begin{aligned}
&\Delta\frac{1}{\lambda}(\text{C}-\text{B}) = 590\ \text{cm}^{-1}\\
&\Delta\frac{1}{\lambda}(\text{E}-\text{D}) = 570\ \text{,,}\\
&\Delta\frac{1}{\lambda}(\text{II}-\text{I}) = 460\ \text{,,}
\end{aligned}\right\}\ \text{Mean. } \Delta\frac{1}{\lambda} = 540\ \text{cm}^{-1}$$

The long and short intervals $\left(\Delta\frac{1}{\lambda} = 1480\ \text{cm}^{-1}\ \text{and}\ 540\ \text{cm}^{-1}\right)$ between the absorption bands of the first series, calculated by the writer, as shown in the table, agree quite well with the results obtained by Henri and Steiner.

2. Δ^1-Dihydronaphthalene

The Δ^1-dihydronaphthalene used in this experiment was prepared from ac-tetrahydro-β-naphthol by dehydration with potassium hydroxide[1] and purified by distillation with metallic sodium. It shows the following properties; B. p.$=(206-207)$; $d_4^{25}=0.9926$; $n_D^{25}=1.5782$.

The ultra violet absorption spectra of this substance and the wave length and wave number of the absorption bands are shown in Fig. 2 and Table II.

The results given therein, which are different from those obtained by Baly and Tuck[2], show four absorption bands from A to D in the region $\lambda = 3220$Å—2973Å, and correspond to the first series of absorption band of naphthalene, and the absorption band E ($\lambda = 2947$ Å—2445 Å) which is broad and diffused one, corresponds from its nature to the second series. Bands C and D are the most intense and the interval

1. Kimura: These Memoirs, A, **14**, 190 (1931)
2. Jour. Chem. Soc., **93**, 1907 (1908).

Fig. 2

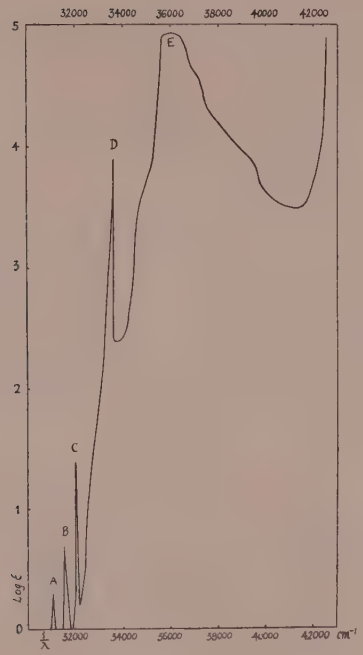


Table II

Band	λ(Å)	$\frac{1}{\lambda}$(cm^{-1})	$\Delta\frac{1}{\lambda}$(cm^{-1})
A	3220	31050	
B	3170	31550	(B—A)=500
C	3125	32000	(C—B)=450
D	2973	33630	(D—C)=1630
E	2947 2775 2445	36040	

of these bands, $\Delta\frac{1}{\lambda}=1630\text{cm}^{-1}$, is the same as the long interval of the first series; another interval, which corresponds to the short one, is also noticed between bands B—A and C—B.

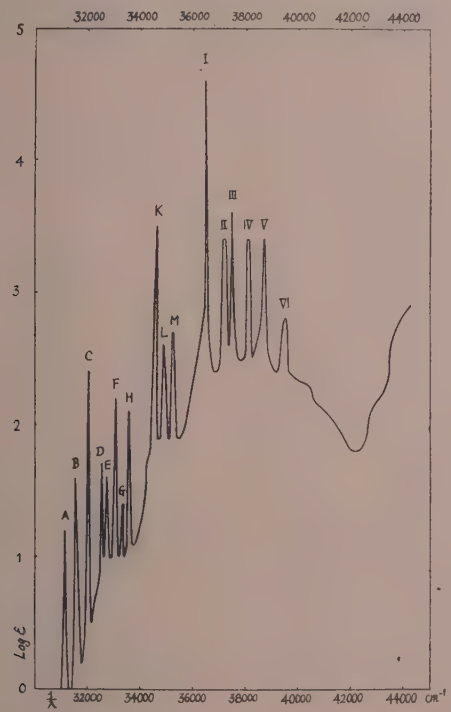
3. Tetrahydronaphthalene

Tetralin from Kahlbaum, purified by distillation with metallic sodium,

and showing the properties B.p.=(204—206); d_4^{25}=0.9675; n_D^{25}=1.5408, was used in the experiment.

In Fig. 3 and Table III, the absorption curves, the wave length and wave number of the absorption bands are shown; these results are not the same as those obtained by Baly and Tuck[1] with tetrahydronaphthalene and α-tetrahydronaphthalene.

Fig. 3



The absorption bands from A to M, appearing in the region λ= 3210 Å—2840 Å, are sharp and distinct and resemble in nature the absorption bands of the first series of naphthalene. Of them, bands A, B, C, F, H and I are the most intense, and the intervals $\Delta\frac{1}{\lambda}$= 1510 cm^{-1} and $\Delta\frac{1}{\lambda}$=500 cm^{-1}, as shown in the Table III, correspond to the long and the short interval of naphthalene. The bands

1. Jour. Chem. Soc., **93**, 1907 (1908).

Table III

Band	λ(Å)	$\frac{1}{\lambda}$(cm^{-1})	$\Delta\frac{1}{\lambda}$(cm^{-1})
A	3210	31150	(F−B)=1550
B	3175	31500	(H−C)=1510
C	3120	32050	(E−A)=1570
D	3073	32540	(K−F)=1570
E	3056	32720	(L−G)=1580
F	3026	33050	(B−A)= 450
G	3005	33280	(C−B)= 550
H	2980	33560	(D−C)= 490
K	2888	34620	
L	2868	34860	
M	2840	35210	
I	2745	36430	
II	2689	37180	
III	2670	37450	
IV	2625	38090	(IV−I)=1660
V	2586	38670	(V−II)=1490
VI	2532	39500	

corresponding to the second series, which appear in the region λ= 2745 Å〜2532 Å, 6 diffused bands from I to VI, have also the interval $\Delta\frac{1}{\lambda}=1500\ \text{cm}^{-1}$.

4. Cis-Octahydronaphthalene

Cis-Octahydronaphthalene was obtained by dehydration of cis-decahydro-β-naphthol, M.p.=105 with $H_2SO_43H_2O$[1], and was purified by distillation with metallic sodium. Its physical properties are as follows: B.p.=(191—191.5); d_4^{25}=0.9135; n_D^{25}=1.4918.

1. These Memoirs, A, **14**, 191 (1931);

Fig. 4

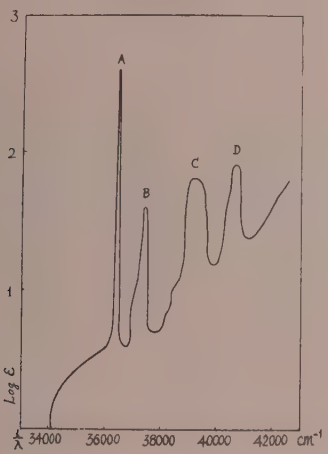


Table IV

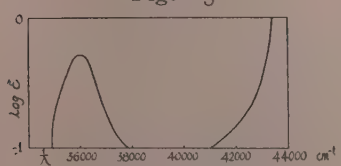
Band	λ(Å)	$\frac{1}{\lambda}$(cm^{-1})	$\Delta\frac{1}{\lambda}$(cm^{-1})
A	2747	36430	
B	2673	37410	(B−A)= 980
C	2550	29220	(C−B)=1810
D	2463	40600	(D−C)=1380

The absorption spectrum of this compound as shown in Fig. 4 and Table IV, was composed only of four broad and diffused bands from A to D, which correspond to the second series of naphthalene and their interval is similar to that measured by the writer with the corresponding bands of tetrahydronaphthalene.

5. Decahydronaphthalene

The decahydronaphthalene used in this experiment was prepared from tetrahydronaphthalene by catalytic reduction under high pressure and high temperature, and purified by treating it with conc. H_2SO_4, alkali and water, and then by distillation on metallic sodium. It shows B.p.= (190—192); d_4^{25}=0.8836; n_D^{25}=1.4738.

Fig. 5



The absorption spectrum of this compound, as shown in Fig. 5, shows a broad, diffused band with its head situated at $\lambda = 2780$ Å $\frac{1}{\lambda} = 35970\ \mathrm{cm}^{-1}$.

In conclusion, the writer wishes to express his sincere thanks to Prof. Dr. S. Komatsu for his kind guidance and valuable suggestions throughout this work and also to Dr. S. Kitashima and Dr. Mrs. S. Kato of the Institute of Physical and Chemical Research of Tokyo, for their generous gift of the Geissler tube used in these experiments.

March 1931,

Laboratory of Organic- & Bio-Chemistry.

On the Definition of Functions by the Recurrence Formula so as to satisfy the Linear Homogeneous Differential Equations of the Second Order

By

Toshizô Matsumoto

(Received September 29, 1931)

1. Legendre polynomials, Bessel functions and many other polynomials commonly known satisfy certain recurrence formulas. These functions are defined as the integrals of certain linear homogeneous differential equations of the second order. Sometimes they are defined as the coefficients of the expansions of certain functions. In general as a consequence of these definitions, those functions satisfy certain recurrence formulas. Now conversely let us define a sequence of functions $\{F_n(x)\}$ by the recurrence formula $F_{n+1}(x)=A_n(x)F_n(x)+B_{n-1}(x)F_{n-1}(x)$ where the sequences of functions $A_1(x)$, $A_2(x)$,....., $A_n(x)$,..... and $B_0(x)$, $B_1(x)$,....., $B_{n-1}(x)$,..... are given, and find the differential equations

$$\frac{d^2F}{dx^2}+\alpha_n(x)\frac{dF}{dx}+\beta_n(x)F=0$$

satisfied by these functions $F_n(x)$.

2. If we give at random two sequences of functions $A_1(x)$, $A_2(x)$,....., $A_n(x)$,..... and $B_0(x)$, $B_1(x)$,....., $B_{n-1}(x)$,..... and put

$$F_{n+1}(x)=A_n(x)F_n(x)+B_{n-1}(x)F_{n-1}(x),\quad n=1,2,.....,$$

then a sequence of functions $\{F_n(x)\}$ is surely defined, provided we give two initial functions $F_0(x)$, $F_1(x)$. This equality is quite a general recurrence formula. But since we give at random the sequence $\{A_n(x)\}$, when only the n first functions $A_1(x)$, $A_2(x)$,....., $A_n(x)$ are given, we can not know the next function $A_{n+1}(x)$. That is $A_n(x)$ is not the analytical expression of n. It is the same with $\{B_{n-1}(x)\}$. The

recurrence formulas commonly used are different at this point. For example Legendre polynomials $P_n(x)$ satisfy the recurrence formula

$$P_{n+1}(x)=\frac{2n+1}{n+1}xP_n(x)-\frac{n}{n+1}P_{n-1}(x),\ n=1,\ 2,\ldots\ldots,$$

so that $$A_n(x)=\frac{2n+1}{n+1}x,\quad B_{n-1}(x)=-\frac{n}{n+1},$$

and they are analytical expressions of n. Therefore in the following we suppose that $A_n(x)$, $B_n(x)$ are given by some analytical expressions of x and n, say

$$A_n(x)\equiv A(x,\ n),$$

$$B_n(x)\equiv B(x,\ n).$$

Then $F_n(x)$ are the solutions of the difference equation

$$F_{\nu+2}=A_{\nu+1}F_{\nu+1}+B_\nu F_\nu.$$

containing the original variable x as a parameter. If $A(x,\ n)$, $B(x,n)$ and the initial functions $F_0(x)$, $F_1(x)$ are polynomials of x, then $F_n(x)$ are also polynomials of x.

3. To construct the linear homogeneous differential equations of the second order satisfied by the functions $F_n(x)$, $F_{n+1}(x)$,....., we put first

$$\left.\begin{aligned}\frac{dF_n}{dx}&=H_nF_n+K_{n-1}F_{n-1}\\ \frac{dF_{n-1}}{dx}&=I_nF_n+M_{n-1}F_{n-1}\end{aligned}\right\}\qquad(1)$$

where H_n, K_{n-1}, I_n, M_{n-1} are certain functions of x. Since the sequence $\{F_n(x)\}$ is already defined, only one of the functions $H_n(x)$ and $K_{n-1}(x)$ is arbitrary. It is the same with the functions $I_n(x)$, $M_{n-1}(x)$. By these simultaneous relations we easily get the differential equation satisfied by $F_n(x)$, namely

$$\left.\begin{aligned}&\frac{d^2F}{dx^2}+\alpha_n\frac{dF}{dx}+\beta_nF=0,\\ \text{where}\quad&\alpha_n\equiv-\left(H_n+M_{n-1}+\frac{K'_{n-1}}{K_{n-1}}\right),\\ &\beta_n\equiv-(H'_n+K_{n-1}I_n)+H_n\left(M_{n-1}+\frac{K'_{n-1}}{K_{n-1}}\right),\end{aligned}\right\}\qquad(2)$$

K'_{n-1}, H'_n being the differential quotients with respect to x of K_{n-1} and H_n respectively.

Next to find the differential equation satisfied by F_{n+1}, first from the equalities

$$\frac{dF_n}{dx} = H_n F_n + K_{n-1} F_{n-1},$$

$$\frac{dF_{n-1}}{dx} = L_n F_n + M_{n-1} F_{n-1},$$

$$F_{n+1} = A_n F_n + B_{n-1} F_{n-1},$$

we have the relations

$$\frac{dF_{n+1}}{dx} = H_{n+1} F_{n+1} + K_n F_n,$$

$$\frac{dF_n}{dx} = L_{n+1} F_{n+1} + M_n F_n,$$

where

$$\left.\begin{aligned} &H_{n+1} \equiv A_n L_{n+1} + M_{n-1} + \frac{B'_{n-1}}{B_{n-1}} \\ &K_n \equiv A_n H_n + B_{n-1} L_n + A'_n - A_n H_{n+1} \\ &L_{n+1} \equiv \frac{K_{n-1}}{B_{n-1}} \\ &M_n \equiv H_n - A_n L_{n+1}. \end{aligned}\right\} \quad (3)$$

Therefore the required differential equation is

$$\left.\begin{aligned} &\frac{d^2F_{n+1}}{dx^2} + \alpha_{n+1}\frac{dF_{n+1}}{dx} + \beta_{n+1} F_{n+1} = 0, \\ \text{where}\quad &\alpha_{n+1} \equiv -\left(H_{n+1} + M_n + \frac{K'_n}{K_n}\right), \\ &\beta_{n+1} \equiv -(H'_{n+1} + K_n L_{n+1}) + H_{n+1}\left(M_n + \frac{K'_n}{K_n}\right). \end{aligned}\right\} \quad (4)$$

4. If we give e. g., K_{n-1}, M_{n-1} as analytical expressions of x and n, then by (1) and (2), α_n is an analytical expression of x and n, say $\alpha_n \equiv \alpha(x, n)$. Yet it is not certain that $\alpha_{n+1} = \alpha(x, n+1)$. The same with β_n. Instead of following up that line of study we shall in the following find the conditions that $\alpha_n = \alpha_{n+1}$.

For $\alpha_n = \alpha_{n+1}$, we have by (2) and (4),

$$H_{n+1} + M_n + \frac{K'_n}{K_n} = H_n + M_{n-1} + \frac{K'_{n-1}}{K_{n-1}}.$$

Putting the values of H_{n+1}, M_n in the left of the equality, by formula (3), we easily get the condition

$$\frac{B'_{n-1}}{B_{n-1}}+\frac{K'_n}{K_n}=\frac{K'_{n-1}}{K_{n-1}},$$

or, integrating, we have

$$B_{n-1}K_n=c_nK_{n-1}, \tag{5}$$

where c_n is constant with respect to x. If the condition be satisfied, we have by the third formula of (3),

$$\frac{K'_n}{K_n}=\frac{I'_{n+1}}{I_{n+1}},$$

or, integrating, we have

$$I_{n+1}=C_nK_n, \tag{6}$$

where C_n is constant with respect to x. c_n and C_n are not independent. For since by (3),

$$I_{n+1}=\frac{K_{n-1}}{B_{n-1}},$$

we have by (6) and (5),

$$C_nK_n=\frac{K_n}{c_n}.$$

Therefore $c_nC_n=1$.

In the same way the condition for $\alpha_{n+1}=\alpha_{n+2}$ may be given by

$$I_{n+2}=C_{n+1}K_{n+1},$$

where C_{n+1} is constant with respect to x. Therefore if the condition (6) be satisfied for n, $n+1$, $n+2$, ..., then $\alpha_n=\alpha_{n+1}=\alpha_{n+2}=$....., i. e., they are independent of the suffixes.

5. For the functions commonly known, the above conditions are always satisfied as is shown in the following list.

Legendre polynomial $P_n(x)$.

$$P_{n+1}=\frac{2n+1}{n+1}xP_n-\frac{n}{n+1}P_{n-1},$$

$$P'_{n+1}=\frac{(n+1)x}{x^2-1}P_{n+1}-\frac{n+1}{x^2-1}P_n,$$

$$P'_n=\frac{n+1}{x^2-1}P_{n+1}-\frac{(n+1)x}{x^2-1}P_n,$$

$$\frac{d^2P_{n+1}}{dx^2}+\frac{2x}{x^2-1}\frac{dP_{n+1}}{dx}-\frac{(n+1)(n+2)}{x^2-1}P_{n+1}=0.$$

The middle two equalities are obtained from the definition of the polynomials,

$$\frac{1}{\sqrt{1-2xz+z^2}}=P_0(x)+P_1(x)z+\ldots\ldots+P_n(x)z^n+\ldots\ldots,$$

$$(|z|<1)$$

by aid of the recurrence formula.

Bessel functions $J_n(x)$.

$$J_{n+1}=\frac{2n}{x}J_n-J_{n-1},$$

$$J'_{n+1}=-\frac{n+1}{x}J_{n+1}+J_n,$$

$$J'_n=-J_{n+1}+\frac{n}{x}J_n,$$

$$\frac{d^2J_{n+1}}{dx^2}+\frac{1}{x}\frac{dJ_{n+1}}{dx}+\left(1-\frac{(n+1)^2}{x^2}\right)J_{n+1}=0.$$

The middle two equalities for integral values of n may also be obtained from the definition of the functions

$$e^{\frac{x}{2}\left(z-\frac{1}{z}\right)}=\sum_{n=-\infty}^{\infty}J_n(x)z^n$$

by aid of the recurrence formula.

This is quite different from *Tchebyscheff's polynomials* $T_n(x)$. They may be defined as the coefficients of the expansion

$$\frac{1-z^2}{1-2xz+z^2}=\sum_{n=0}^{\infty}T_n(x)(2z)^n,$$

and they satisfy the recurrence formula

$$T_{n+1}=xT_n-\frac{1}{4}T_{n-1},\quad n\geqslant 2,$$

and the differential equation

$$\frac{d^2T_{n+1}}{dx^2}-\frac{x}{1-x^2}\frac{dT_{n+1}}{dx}+\frac{(n+1)^2}{1-x^2}T_{n+1}=0.$$

To determine four functions such as

$$\left.\begin{aligned}\frac{dT_n}{dx}&=H_nT_n+K_{n-1}T_{n-1}\\ \frac{dT_{n-1}}{dx}&=I_nT_n+M_{n-1}T_{n-1}\end{aligned}\right\},$$

if we treat as in the cases of $P_n(x)$ and $J_n(x)$, we differentiate the definitional equation with respect to x. Then

$$2z\sum_{n=0}^{\infty}T_n'(2z)^n=(1-2xz+z^2)\sum_{n=0}^{\infty}T_n'(2z)^n.$$

Equating the coefficients of n^{th} degree in $2z$, we have

$$T_{n-1}=T_n'-xT_{n-1}'+\frac{1}{4}T_{n-2}', \quad n\geqslant 2.$$

By the recurrence formula we have

$$T_n'=T_{n-1}+xT_{n-1}'-\frac{1}{4}T_{n-2}',$$

which is identical with the preceding equality. Hence we can not determine the functions H_n, K_{n-1}, I_n, M_{n-1}. In this case, since

$$T_n(x)=\left(\frac{x+\sqrt{x^2-1}}{2}\right)^n+\left(\frac{x-\sqrt{x^2-1}}{2}\right)^n, \quad n\geqslant 1,$$

we have

$$\begin{aligned}\frac{dT_n}{dx}&=n\frac{1+\frac{x}{\sqrt{x^2-1}}}{2}\left(\frac{x+\sqrt{x^2-1}}{2}\right)^{n-1}\\ &\quad+n\frac{1-\frac{x}{\sqrt{x^2-1}}}{2}\left(\frac{x-\sqrt{x^2-1}}{2}\right)^{n-1}\\ &=\frac{n}{\sqrt{x^2-1}}\left\{(x+\sqrt{x^2-1})^n-(x-\sqrt{x^2-1})^n\right\},\end{aligned}$$

putting $\equiv H_nT_n+K_{n-1}T_{n-1},$

therefore $$\begin{aligned}&=\left(H_n+\frac{2K_{n-1}}{x+\sqrt{x^2-1}}\right)\left(\frac{x+\sqrt{x^2-1}}{2}\right)^n\\ &\quad+\left(H_n+\frac{2K_{n-1}}{x-\sqrt{x^2-1}}\right)\left(\frac{x-\sqrt{x^2-1}}{2}\right)^n.\end{aligned}$$

To satisfy this equality, we may choose H_n and K_{n-1} in several ways. But assume for example

$$\left.\begin{aligned} H_n+\frac{2K_{n-1}}{x+\sqrt{x^2-1}}&=\frac{n}{\sqrt{x^2-1}}\\ H_n+\frac{2K_{n-1}}{x-\sqrt{x^2-1}}&=-\frac{n}{\sqrt{x^2-1}}\end{aligned}\right\},$$

then we have

$$H_n=\frac{nx}{x^2-1},\quad K_{n-1}=-\frac{n}{2(x^2-1)},$$

so that we have

$$\left.\begin{aligned} T'_{n+1}&=\frac{(n+1)x}{x^2-1}T_{n+1}-\frac{n+1}{2(x^2-1)}T_n,\quad (n\geqslant 1)\\ \text{and hence}\quad T'_n&=\frac{2n}{x^2-1}T_{n+1}-\frac{nx}{x^2-1}T_n,\quad (n\geqslant 0)\end{aligned}\right\}. \tag{7}$$

Here we have

$$I_{n+1}=\frac{2n}{x^2-1},\quad K_n=-\frac{n+1}{2(x^2-1)},$$

such that $I_{n+1}:K_n$ is constant with respect to x. Therefore, as we have proved, $\alpha_n=\alpha_{n+1}$. In our present case, the legitimacy of the equalities (7) can easily be verified, since the differential equation is previously given. But if as we have proposed, the sequence of functions $\{F_n(x)\}$ be only defined and the differential equations to be satisfied by them are not given, it seems to be useful to test the ratio $I_{n+1}:K_n$ for the verification of $\alpha_n=\alpha_{n+1}$.

6. Hitherto we have considered the coefficient α_n of the differential equation to be independent of n. The functions which satisfy the differential equations with such a condition seem to play a special rôle just as in the previous examples the functions commonly known satisfy the differential equations with the same condition.

If α_n is independent of n, several special properties would perhaps be displayed. In the following I shall consider the zeros of the functions $F_n(x)$ supposed to satisfy the differential equations

$$\frac{d^2F_n}{dx^2}+\alpha\frac{dF_n}{dx}+\beta_nF_n=0 \tag{8}$$

respectively where $\alpha(x)$ is independent of n and β_n is an analytical expression of x, n real. We shall conclude that often the zeros of $F_n(x)$ change monotonely with n. This seems to be peculiar to the class of these sequences of functions.

Putting $u(x)\equiv e^{\frac{1}{2}\int a\,dx}$,

$$V_n\equiv uF_n, \tag{9}$$

V_n satisfy the following differential equation transformed of (8)

$$\left.\begin{aligned}&\frac{d^2V_n}{dx^2}+\varphi_n(x)V_n=0,\\ \text{where}\quad &\varphi_n(x)\equiv\beta_n-\frac{a'}{2}-\frac{a^2}{4}.\end{aligned}\right\} \tag{10}$$

Differentiating (10) with respect to n,

$$\frac{d^2}{dx^2}\left(\frac{\partial V_n}{\partial n}\right)+\varphi_n\frac{\partial V_n}{\partial n}+\frac{\partial\varphi_n}{\partial n}V_n=0. \tag{11}$$

Multiplying (10) by $\frac{\partial V_n}{\partial n}$, (11) by V_n and substructing side by side, we have

$$\frac{\partial V_n}{\partial n}\frac{d^2V_n}{dx^2}-V_n\frac{d^2}{dx^2}\left(\frac{\partial V_n}{\partial n}\right)=\frac{\partial\varphi_n}{\partial n}V_n^2,$$

or

$$\frac{d}{dx}\left\{V_n\frac{d}{dx}\left(\frac{\partial V_n}{\partial n}\right)-\frac{\partial V_n}{\partial n}\frac{dV_n}{dx}\right\}=-\frac{\partial\varphi_n}{\partial n}V_n^2.$$

If we put $f_n(x)\equiv\frac{\partial F_n(x)}{\partial n}$, $f_n'(x)\equiv\frac{\partial^2F_n(x)}{\partial n\partial x}$,

and remember (9) after integration, the above equality becomes

$$u^2(F_nf_n'-f_nF_n')\Big|_a^b=-\int_a^b\frac{\partial\varphi_n}{\partial n}u^2F_n^2dx, \tag{12}$$

with a proper choice of the limits of the integration, in which the integral of the right-hand side is supposed to exist. Assume $u(0)=0$ or $F_n(0)=F_n'(0)=0$; let $x_0>0$ be a simple root of $F_n(x)=0$, where $u(x_0)\neq0$, then we have by (12)

$$-u^2(x_0)f_n(x_0)F_n'(x_0)=-\int_0^{x_0}\frac{\partial\varphi_n}{\partial n}u^2F_n^2dx.$$

Since by (10)

$$\frac{\partial\varphi_n}{\partial n}=\frac{\partial\beta_n}{\partial n},$$

we have $f_n(x_0)=\frac{1}{u^2(x_0)F_n'(x_0)}\int_0^{x_0}\frac{\partial\beta_n}{\partial n}u^2F_n^2dx.$

From $F_n(x_0)=0$, we have

$$\frac{dx_0}{dn} = -\frac{f_n(x_0)}{F_n'(x_0)}.$$

Hence we have

$$\frac{dx_0}{dn} = -\frac{1}{u^2(x_0)F_n'(x_0)} \int_0^{x_0} \frac{\partial \beta_n}{\partial n} u^2 F_n^2 dx.$$

When $\frac{\partial \beta_n}{\partial n} < 0$, we may conclude that x_0 increases with n.

The above reasoning is of course inadequate, yet we are convinced that a special rôle is played by the property that $u(x)$ and hence $\alpha(x)$ is independent of n.

Quantitative Spectrum Analysis, Part III and IV

By

Arata Iwamura

(Received October 19, 1931)

Part III. Quantitative Emission-Spectrum Analysis of Cadmium contained in Zinc Oxide

1. Sample electrodes and standard electrodes.

For the purpose of estimating cadmium contained in zinc oxide by means of the emission-spectrum, the oxide was first transformed into tablets which were used as the electrode in the same manner as was described in the case of determining lead contained in zinc oxide[1]. The standard electrodes containing varying amounts of cadmium were prepared by mixing known amounts of cadmium carbonate and zinc oxide and transforming the mixture into tablets.

2. The apparatus used and the method of experiment.

The experiment was conducted in a manner analogous to that in the determination of lead in zinc oxide, with the apparatus described in the previous reports.[1]

3. Sensitiveness of spectrographic analysis.

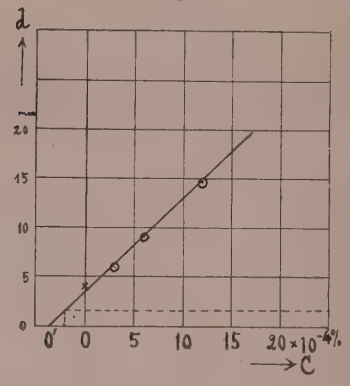
The determination of the sensitiveness of the quantitative spectrum analysis of cadmium contained in zinc oxide was also conducted in the same manner as in the analysis of lead contained in zinc oxide. The relation between the concentration of cadmium contained in zinc oxide and the photographic densities of the Cd line at $\lambda = 2288$Å is shown in the following table, figure and the corresponding micro-photometer records.

1. These Memoirs, **14**, 49 (1931).

d_{mm}	Conc. of Cd
4.2	x %
6.0	0.0003
9.2	0.0006
14.7	0.0012
11.6	0.0024
15.5	0.0090

(See PL. I. 1)

Fig. 1



The point at which the elongation of this curve and the horizontal dotted line (which shows the density of the back ground of the plate) parallel to the abscissa intersect, corresponds to the concentration of cadmium in zinc oxide, which gives the limit of density of the cadmium line observable by the microphotometer, that is to say, the minimum limit of detectable amount. The value thus found was 1.5×10^{-4} % under the conditions of the experiment. The value may, however, vary within certain limits depending upon the condition of the photographic plate, and the method of developing etc.

The intersection of the elongation of the density-concentration curve and the abscissa denotes the true zero-point, that is to say, the zero-point of the coordinates should be displaced by 00′, 00′ denoting the initial concentration of cadmium contained in zinc oxide. The initial concentration of cadmium was thus found graphically to be 3.6×10^{-4} %.

4. Influence of acids used for cementing zinc oxide.

The influence of hydrochloric, sulphuric and nitric acids used in cementing the zinc oxide at the concentration of 0.050 % of Cd was determined by using the cadmium line $\lambda = 2288$Å, and the densities given by the microphotometer were found as follows:

	chloride (a)	sulphate (b)	nitrate (c)
d_{mm}	15.3	9.3	9.1

It will be seen that though the densities are of the same order of magnitude, hydrochloric acid gives the most sensitive result. (See PL. I. 2 & 3).

5. Influence of cathions.

Those elements which have some spectral lines in the vicinity of the cadmium line at $\lambda = 2288$Å are as follows:

λ	Origin	F (intensity)	λ	Origin	F (intensity)
2298.2	Fe	1	2289.0	Fe	—
2297.8	Fe	—	2288.1	As	3
2294.7	Cd	4	2287.6 / 2287.3	Fe	—
2293.85 / 2294.30	Cu	5	2286.7	Sn	3
2292.5	Fe	—	2280.2 / 2279.9	Fe	—
2291.1	Fe	—	2279.6	Ni	—
2290.6	Fe	—	2276.6	Bi	2
2290.0	Ni	—			

Now, each of the above mentioned elements was added in small varying amounts, to a definite quantity of a zinc oxide sample containing a definite amount of cadmium till the concentration of the added element became 3 mol in 1000 mol of zinc oxide, and the mixture was cemented into electrodes, sparked and spectrographed as usual. The abovementioned elements were observed to give no detectable lines interfering with the cadmium line, $\lambda = 2288$Å, and therefore it became evident that the addition of these elements in the concentration mentioned above would influence neither the back-ground nor the cadmium line.

6. Examples of analysis.

The experiments for determining cadmium in zinc oxide ranging from 0.001 to 0.02 % were performed with the results described below, and one of the spectrograms and its microphotometer records are shown in the plate. (PL. I. 4 & 5)

Purely chemical analysis of cadmium contained in zinc oxide in a very small quantity would probably be a painstaking work and the results could not be trustworthy, as the tediousness of the process might introduce many sources of error.

The spectrographic method will be a more convenient and sensitive substitute for that method.

Ex. 1

The content of cadmium in the sample to be analysed is denoted by S, the mean value of which was found to be 0.00136 %.

The content of cadmium initially contained in zinc oxide used in

the present experiment was found to be 3.6×10^{-4} % as was stated in 3. Hence, the total content of cadmium was calculated by adding this amount to that of cadmium which was added for the purpose of preparing sample electrodes with varying cadmium concentrations.

Ex. 1.

S=0.00136 %

% Cd	d_{mm} λ=2288Å
0.00066	—
S	—
0.00096	5.8
S	0.4 > 3.6
0.00156	11.0 > 1.6
S	—
0.00276	—
S	—
0.00516	—

(See PL. I. 4 & 5)

by proportion we get, $60 \times \frac{1.6}{5.2} = 18.5 \fallingdotseq 19$

$\therefore$ S=0.00156−0.00019=0.00137

$\Delta = 100 \times \frac{1}{136} = +0.7^{+}$ %

Ex. 2.

S=0.01536 %

% Cd	d_{mm} λ=2288Å
0.03746	—
S	—
0.01896	24.2
S	19.8 > 4.4
0.00966	8.2 > 11.6
S	—
0.00496	—
S	—
0.00266	—

(See PL. I. 6)

by proportion we get, $930 \times \frac{4.4}{16.0} = 256$

$\therefore$ S=0.01896−0.00266−0.01640

$\Delta = 100 \times \frac{1640-1536}{1536} = +6.8-$ %

Two more experiments were performed, and the microphotometer records shown in PL. I. 7 and 8, and the values of S described below were obtained.

Plate I

Ex. 3. S 0.02012%, for the theoretical value, 0.01921%
Ex. 4. S 0.01135% „ „ „ 0.01082%

7. Comparison of the results of spectrographic analysis with the theoretical.

Let S denote the value of cadmium spectrographically obtained, T, the theoretical value and Δ the percentage deviation from the theoretical values.

No.	S	T	Δ %
I	0.00137	0.00136	$+0.7^{+}$
II	0.01640	0.01536	$+6.8^{-}$
III	0.02012	0.01921	$+4.7^{+}$
IV	0.01135	0.01082	$+4.9^{-}$

As is shown in the above table, the spectrographic results coincide with the theoretical value fairly well, the percentage error lying between $+0.7^{+}$ and $+6.8$.

Summary

1. Solid conducting electrodes consisting of a zinc oxide sample containing cadmium were prepared for the purpose of the quantitative emission-spectrum analysis.

2. The sensitiveness of the method for estimating cadmium contained in zinc oxide was determined to be 1.5×10^{-4}% under the conditions used in the experiments.

By elongation of the density-concentration curve, the initial concentration of cadmium contained in zinc oxide was found to be 3.6×10^{-4} %.

3. The spectrographic values obtained in the analysis were found nearly coincident with the theoretical values, the divergency being always within the limit of permissible error.

Part IV. Quantitative Emission-Spectrum Analysis of Copper contained in Lead

1. With the object of ascertaining how far the determination of a minute quantity of copper existing in an organic compound may be performed spectro-graphically the writer tried to change the copper combining with an organic radical into the form of an alloy with lead, in the manner described below, and to use it as the electrode in the quantitative emission-spectrum analysis.

2. Preparation of sample electrodes.

As the organic copper compound, copper benzoinoxime $C_{14}H_{10}O_2NCu$ was taken. Now 10.0 grams of pure lead sheet cut in small pieces were melted in a porcelain crucible in the presence of a reducing agent such as cane-sugar and 4.5 mg. of coppor benzoinoxime were added to it and well mixed, when the organic compound was decomposed leaving copper as an alloy. Another 10.0 grams of lead were then added and stirred well with a porcelain rod. It was cast quickly, hammered and cut in pieces so as to form cubes of 3mm. × 1mm. × 20mm. The lead cubes containing 0.005% copper thus obtained were used as electrodes. In the same way, lead electrodes containing varying amounts of copper were prepared. Other metals such as cadmium or zinc may also be used instead of lead for the same purpose.

3. Reproducibility of the spectrograms.

The spectrograms of lead containing copper were found to be quite reproducible as is shown in PL. II. 1.

4. Sensitiveness.

The sensitiveness of the copper analysis was experimentally determined as in the analysis of lead contained in zinc oxide[1]. (PL. II. 2)

The densities of the copper lines at $\lambda=3248$Å and 3274Å were photometrically determined by Moll's microphotometer and the sensibility of the line at $\lambda=3274$Å was determined as is shown in the accompanying figure and the table. Microphotometrical records are also shown reproduced in PL. II. 3.

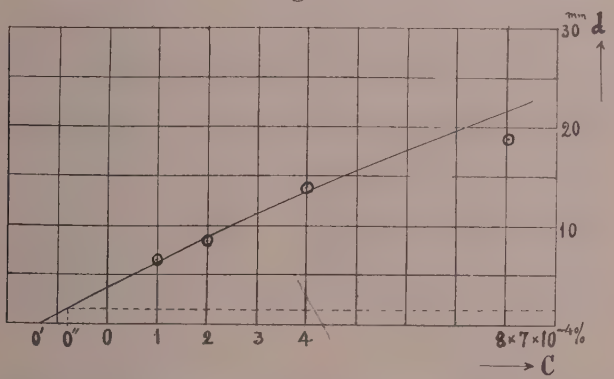
The determination of the initial concentration of copper contained in the sample was carried out in the same way as was mentioned in Part III.

---

1. These Memoirs, **14**, 51, (1931).

% Cu in Pb	d	
	$\lambda = 3247.5$Å	$= 3274.0$Å
0.0007	—	6.7mm
0.00146	7.9	8.1
0.0029	13.2	13.9
0.00586	—	18.7
0.01172	22.3	—
0.02344	23.5	18.7
0.0469	32.3	20.6
0.0938	33.1	21.0

Fig. 2.



Initial conc. of Cu in Pb $= 9.1 \times 10^{-4}\%$ (denoted by oo′ in the above figure). Sensitiveness $= 3.5 \times 10^{-4}\%$ (denoted by o′o″ in the above figure).

5. Examples.

Ex. 1.

S = 0.01641 %

Cu %	d_{mm} $\lambda = 3274$Å
S	—
0.02431	10.4
S	5.8 > 4.6
0.01261	4.1 > 1.7

(See PL. II. 4)

by proportion we get

$S = 0.01261 + 0.00316 = 0.01577$

$$\Delta = 100 \times \frac{1641 - 1577}{1641} = 100 \times \frac{64}{1641}$$

$\Delta = -3.9\%$

Ex. 2.

S=0.07091%

Cu %	d_{mm} $\lambda=3274\mathring{A}$
S	—
0.09466	18.2
	>3.2
S	15.0
	>4.5
0.04779	10.5

(See PL. II. 5)

by proportion we get

S=0.04779+0.02739=0.07518

$$\Delta=100\times\frac{427}{7091}$$

$\Delta=+6.0\%$

Ex. 3.

S=0.15721%

Cu %	d_{mm} $\lambda=3274\mathring{A}$
S	—
0.18841	39.6
	>2.5
S	37.1
	>4.0
0.09466	33.1

(See PL. II. 6)

by proportion we get

S=0.09466+0.05825=0.15291

$$\Delta=100\times\frac{430}{15721}=2.7$$

$\Delta=-2.7\%$

6. Comparison of the results of spectrographical analysis with the theoretical value.

Let S denote the value of copper obtained spectrographically, T the theoretical value, and Δ the percentage deviation from T.

No.	S	T	Δ %
I	0.01577	0.01641	−3.9+
II	0.07518	0.07091	+6.0+
III	0.15291	0.15721	−2.7+

As is shown in the above table, the spectrographical values coincide tolerably well with the theoretical value, the percentage deviation ranging between −2.7 and +6.0%.

Summary

1. Copper contained in lead was spectrographically analysed with fairly good results.
2. The sensitiveness of the method was found to be 3.5×10^{-4}%.

The initial concentration of copper contained in the so-called pure lead sheet was found to be 9.1×10^{-4} %.

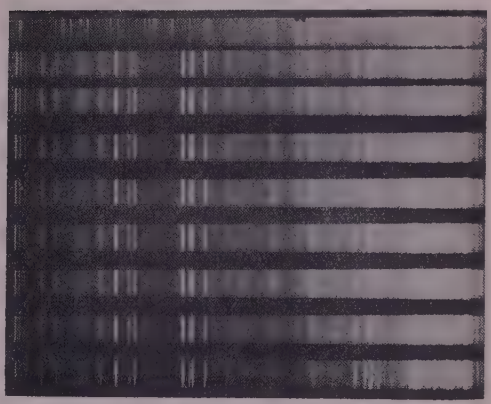
3. It was experimentally confirmed that minute quantities of copper combining with an organic radical might be directly transformed into an alloy with pure lead, cadmium or zinc and the resulting alloys might serve as the electrode for the quantitative spectrographic analysis of the metal.

In conclusion, the writer wishes to express his sincere thanks to Prof. M. Matsui, and Prof. M. Kimura, of the Faculty of Science, K. I. U. for their valuable advice and encouragement.

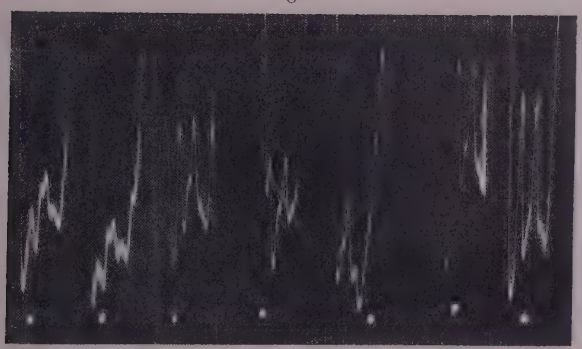
Plate II

1

2



3



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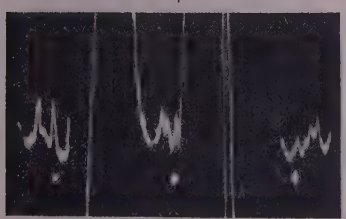

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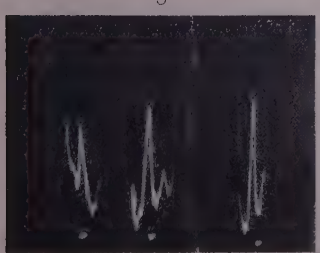

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